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Report DAAK70-85-C-0092

# HYDROGEN PRODUCTION FROM LIQUID HYDROCARBONS DEMONSTRATION PROGRAM

J.B. O'Hara, T.K. Chow, and J.K. Ling
The Ralph M. Parsons Company
100 West Walnut Street
Pasadena, California 91124

1 September 1986

Final Technical Report
Period 26 August 1985 to 1 September 1986

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Prepared for:

BELVOIR RESEARCH, DEVELOPMENT AND
ENGINEERING CENTER
DIRECTORATE FOR LOGISTIC SUPPORT
STRBE-FGC
Fort Belvoir, VA 22060-5606

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes a process configuration which has the potential to produce a minimum of 0.365 pound of hydrogen per pound of feed diesel consumed. The hydrogen-containing product is a suitable fuel for a phosphoric acid fuel cell power plant. A 2 mole per hour (hydrogen) demonstration plant was designed, constructed and started up. Results are summarized.

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## SUMMARY

The Air Force now uses diesel engine generators as sources of heat and
electricity at selected remote sites. Simultaneously, it has investigated
alternative cogeneration candidates that offer improved reliability,
maintainability, and economics. One system that shows high potential is a
phosphoric acid fuel cell (PAFC) power plant consisting of a fuel conditioner
to convert logistic fuels such as DF-2, DF-A, and JP-4 to a hydrogen-rich gas,
the PAFC to convert the hydrogen to direct current electrical power plus heat,
and a power conditioner to convert the direct current power to alternating
current.

The objective of the project work reported here was to define, and
demonstrate, a fuel conditioner to meet performance criteria established for
the Air Force Remote Site Fuel Cell Power Plant program. Key criteria included
high fuel-to-hydrogen conversion efficiency, rapid startup and load following
capability, and minimum water consumption during operations.

A preliminary process design was developed that has the potential to convert
logistic fuels to a hydrogen-rich fuel gas suitable for feed to a PAFC and
meet the project performance criteria. Key elements of the "hybrid" design
included (1) a high temperature steam reformer (HTSR) to convert approximately
55% of the carbon content of the feed logistic fuel to oxides of carbon
(carbon monoxide and carbon dioxide) and (2), an autothermal reformer (ATR) to
convert the remainder of the hydrocarbon feedstock to a mixture of hydrogen
and carbon oxides. Other processing steps included two shift conversion units
to increase the ratio of hydrogen-to-carbon monoxide, a desulfurization step
to reduce the sulfur content of the product fuel gas to less than 10 parts per
million by weight (ppmw), and ancillaries to assure high thermal efficiency
and high efficiency in converting logistic fuels to hydrogen.

A demonstration plant (DP) capable of producing 2 pound moles per hour
(mole/hr) of hydrogen at a concentration of 50% volume minimum, dry basis, was
designed and equipment procurement and construction completed in a 4-month
period. The DP was commissioned, an operating manual prepared, operators
trained, and the DP was started. Limited experimental data was obtained during
a 17 hour test run before a forced shutdown. Principal reasons for shutdown
included failures of an electrically heated steam superheater and the
autothermal reformer (ATR) high temperature electrical heaters.

Analysis of project results led to the following conclusions:

(1)  A process design has been developed that has the potential to achieve
     project goals. This process configuration uses sour reforming to
     process the high sulfur logistic fuels feedstock followed by shift
     reaction and desulfurization.

(2)  Additional operations are required to adequately demonstrate the
     performance of the process configuration. The one month's operating
     time was not adequate because of startup problems primarily caused by
     high temperature electrical heaters.

(3)  The results of a 17 hour run indicate that the DP can produce
     hydrogen-containing product gas with less than 1 ppmv hydrogen
     sulfide.

(4)  Product hydrogen concentration was of the order of 35 mole percent.
     Contaminants exhibiting higher-than-design concentrations included
     methane, carbon monoxide, and nitrogen. Control of these constituents
     as described below will produce a product gas with at least 53%
     hydrogen, which will meet project objectives:

     (a)  Convert all methane to oxides of carbon and hydrogen in the HTSR
          and ATR.

(b) Convert 90% of the carbon monoxide to hydrogen by reaction with steam in the shift reactors.

(c) Reduce the air feed rate to the ATR.

Each of the above changes are achievable.

(5) Failures of high temperature electrical heaters caused forced shutdown of th DP. Design deficiencies of the ATR contributed to failure of the ATR electrical heaters.

(6) Equipment modifications/additions/repairs have been defined that are judged adequate to provide confidence that the DP can operate reliably to demonstrate the performance of the process configuration.

(7) Candidate materials of construction have been defined for the 1800°F-plus operation in sulfur-containing environments. These materials performed satisfactorily for the brief operating period.

(8) Solids, tentatively identified as naphthalene and related compounds, collected in the product gas exit area, causing a malfunction of the product gas meter. To eliminate/control these compounds, oxidation conditions must be controlled in the process and procedures incorporated to assure delivery of clean product gas to the fuel cell.

We recommend that the DP be modified and improved as defined in Section 11 of this report and that operations be resumed to demonstrate that the fuel conditioner process configuration tested is capable of efficiently and reliably converting logistic fuels to a specification hydrogen-rich gas stream suitable for use as fuel for a PAFC.

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PREFACE

The work reported here is one portion of the Air Force Remote Site Fuel Cell
Power Plant program whose objective is to demonstrate logistic fueled fuel
cell power plants at a remote site in Alaska in the early 1990s. The prime
objective of Parsons work summarized in this report is to demonstrate the
performance of fuel processor technology having the potential to form an
integral part of fuel cell power plants that are more reliable, and offer
lower lifecycle cost, than the diesel-engine cogeneration systems now used in
Alaskan remote site radar installations.

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# SECTION 1

## INTRODUCTION

The work reported here represents a contribution to the U.S. Air Force Remote Site Fuel Cell Power Plant program. The objective was to demonstrate viable performance of a technology to convert liquid fuels JP-4, DF-2, and DF-A to a hydrogen-rich gas stream suitable for use in a phosphoric acid fuel cell (PAFC) and to make the demonstrated process available for future competitive procurement by the Government.

The work defines, and tests performance of, a process technology potentially capable of achieving the above-stated objectives at a remote Alaskan site. DF-2 was used as the liquid hydrocarbon feedstock for design and operations testing because it represents the most difficult of the three candidate fuels to process. Satisfactory performance with DF-2 will provide the basis for design/operation of fuel conditioners capable of processing DF-A and JP-4.

The performance requirements for the fuel conditioner are more demanding than the corresponding requirements for industrial hydrogen plants. Key added challenges consist of:

(1) A logistic fuel, as typified by DF-2, is more difficult to process than lower molecular weight historical industrial hydrogen plant feedstocks because DF-2 characteristics include:

(a) Significantly higher average boiling point.

(b) Higher sulfur content.

(c) Presence of complex high boiling point antioxidants, cetane improvers, and corrosion inhibitor additives.

(d) High propensity to form carbon.

(2)  Required rapid startups from cold standby condition to full hydrogen delivery.

(3)  Rapid electrical load-following transient capability.

(4)  High hydrogen-from-fuel feedstock production efficiency.

Processing these high boiling, high sulfur, complex, and variable chemical composition feedstocks to meet the indicated stringent performance criteria places the fuel conditioner at the cutting edge of hydrogen production technology.

The following sections will describe the basis for selection of the preferred process configuration; the process and mechanical design of the demonstration plant (DP); the safety and reliability factors for the process plant; the plant's construction, commissioning, startup, and operations; and interpretation of the operating results relative to the project objective. Conclusions and recommendations are also presented.

These results provide the basis for future work to design, construct, and operate prototype fuel conditioners that will achieve the Remote Site Fuel Cell Power Plant program objectives.

SECTION 2

PROCESS SELECTION

A. SELECTION CRITERIA

There are approximately 120 hydrogen producing facilities in the U.S. with a
combined production capacity of about 100 billion scfd/yr. Feedstocks range
from natural gas to naphtha. These hydrogen plant feedstocks have nil sulfur
content. End uses for hydrogen include ammonia and methanol manufacture,
hydrocracking, hydrotreating, hydrodesulfurization, chemical, pharmaceutical,
food, metal, and electronic industries. Unit plant capacities range from 0.1
to 75 million scfd.

The industrial experience available from the above cited hydrogen plants
provides limited basis for preferred facilities design and operation of the
demonstration plant (DP). A key distinguishing factor for the DP is that
sulfur contaminants in the higher boiling feedstocks (for example, end points
to 786°F for DF-2) make it difficult and costly to completely remove the
sulfur by conventional means and then produce hydrogen using standard "sweet"
reforming catalysts and conditions. There is, therefore, an incentive to
investigate use of an alternative process scheme using sulfur-resistant
catalysts capable of operating at high temperatures. The high temperature and
high sulfur content environment requires specialized alloys and equipment
fabrication techniques.

Other differences between conventional hydrogen manufacture and the DP design
were summarized in Section 1.

All factors were included in the design and process selection criteria. The
fuel processor capabilities must include:

    (1)  Processing DF-2, DF-A, and JP-4 petroleum feedstocks interchangeably.

(2) Producing a hydrogen product stream with the following specifications for use in a phosphoric acid fuel cell (PAFC):

| Component | Percent by Volume, Dry Basis |
|---|---|
| Hydrogen | 50, minimum |
| Carbon monoxide | 1, maximum |
| Sulfur | 10 ppmw, maximum |

(3) Achieving a minimum hydrogen yield of 0.365 lb per pound of fuel consumed. The ultimate target is 0.42 lb.

(4) High turndown and quick transient response capabilities.

(5) Operating with minimum water consumption.

(6) Operating at high reliability with minimum operation supervision.

(7) Operating with minimum maintenance.

(8) Attaining maximum integration with a PAFC.

B.  SELECTION RATIONALE

Partial oxidation (POX) and catalytic steam reforming are commercially proven technologies for manufacturing hydrogen from light hydrocarbon feedstocks. For feedstocks heavier than naphtha, the POX process is commercially used.

For the POX process, either air or pure oxygen can be used as the oxidant. Because nitrogen is the majority constituent of air, the POX effluent gas will be diluted by nitrogen when air is the oxidant, resulting in a hydrogen and carbon monoxide content below 50%. To ensure a greater than 50% hydrogen and carbon monoxide content in a POX effluent, pure oxygen or oxygen-enriched air must be used. This necessitates production of oxygen in the plant, which adds cost and complexity to the hydrogen manufacturing process. Also, the hydrogen-from-fuel efficiency target cannot be readily achieved using POX technology

exclusively. A process configuration using only POX technology was, therefore, rejected for this project.

The catalytic steam reforming process is a potential candidate for the fuel processor. However, commercial reforming uses essentially sulfur-free light hydrocarbon feedstocks. The conventional steam reforming catalysts have very low sulfur tolerance and operating temperatures are in the 1500°F to 1600°F temperature range.

For heavier hydrocarbon feedstocks, a catalyst that is sulfur resistant and operates at higher temperatures is required. The sulfur resistant catalyst eliminates the costly, complex, and commercially difficult total sulfur removal process step for the heavy feedstock. A high operating temperature catalyst is required to minimize formation of hydrocarbons heavier than methane in the product gas.

The project performance criteria demands minimum fuel, steam, and catalyst use, plus minimum unconverted methane in the product stream. Current information indicates that use of the high temperature steam reformer (HTSR) as the sole process step to convert DF-2 to a hydrogen and carbon oxides mixture will not economically meet the target project performance standards.

As a result of the above analyses, the "hybrid" combination of HTSR plus autothermal reformer (ATR) was selected to reduce the methane leakage to an acceptable level in the hydrogen and carbon oxides production step while retaining practical levels of temperature, steam rate, and catalyst volume. The HTSR is used to convert the DF-2 to a mixture containing hydrogen and carbon oxides plus methane and lesser amounts of higher molecular weight hydrocarbons. The residual hydrocarbons contained in the HTSR effluent are then converted to additional hydrogen and carbon oxides by contact with air and catalyst at elevated temperature in an ATR. This combined process configuration has the potential to meet the project's performance goals.

The proprietary under-development Toyo Engineering Corporation (TEC) catalyst T-12 offers the potential advantages of being sulfur resistant and capable of

operating at high temperature. It was chosen for use in the catalytic steam reforming step. Similarly, the TEC T-48 catalyst has proven to be sulfur resistant and effective for the ATR reforming step and was, therefore, selected for that use.

Heat required for endothermic reaction in the ATR is supplied by burning part of the HTSR effluent with air. The quantity of air used is controlled to assure meeting the product hydrogen concentration specification of 50 mole percent, minimum.

SECTION 3

PROCESS DESIGN

A. PROCESS DESCRIPTION

The process configuration is shown in Fig 1. The six key process steps are:

(1) Feed preparation.

(2) High temperature steam reformer (HTSR)

(3) Autothermal reformer (ATR).

(4) First stage shift reactor.

(5) Second stage shift reactor.

(6) Desulfurizer.

Each of these process units is described in the following paragraphs.

1. Feed Preparation Section

The objective of this process section is to produce a vapor mixture of steam and DF-2 at the correct molar steam-to-carbon (s/c) ratio, temperature, and pressure for feed to the catalyst section of the HTSR, 1-1401, without forming carbon. This is done by injecting an atomized stream of liquid DF-2 into superheated steam. The resulting fuel/steam mixture enters the HTSR catalyst bed at approximately 970°F.

The DF-2 has a nominal molecular weight of 210, contains approximately 86% carbon by weight, has an end point up to 780°F, and a sulfur content up to 0.7% by weight. The demonstration plant (DP) was designed to accommodate mole s/c ratios of 3.0 to 6.0 in the HTSR.

2. High Temperature Steam Reformer (HTSR)

The HTSR converts the majority of the high molecular weight hydrocarbons contained in the DF-2 to hydrogen, carbon oxides ($CO_x$), and methane.

The HTSR consists of an electrically heated regenerative tube catalytic converter as depicted in Fig. 2. The catalyst is Toyo Engineering Corporation (TEC) T-12. This catalyst is contained in an annular space located between the outer tube, which is externally electrically heated, and an inner tube that transports the catalytic bed effluent out of the HTSR reactor while simultaneously transferring heat to the annular catalytic bed. Operating conditions are summarized in Table 1, to be discussed later in this report section.

Characteristics of catalysts used in the HTSR, plus other process units, are listed in Table 2.

The conversion of DF-2 carbon content to carbon oxides (carbon monoxide plus carbon dioxide) in the HTSR is approximately 55%, with the remainder of the carbon in the form of methane plus minor amounts of higher molecular weight short chain hydrocarbons. The HTSR product is the feed to the ATR, 1-2501.

3.   Autothermal Reformer (ATR)

The ATR, 1-2501, selectively converts residual hydrocarbons contained in the HTSR effluent to a mixture of carbon oxides and hydrogen. This is done in a refractory lined catalytic convertor illustrated in Fig. 3. TEC proprietary catalyst T-48 is used, plus a minor amount of T-12 catalyst. The required endothermic heat of reaction is supplied by combustion of a portion of the feed stream with air supplemented by high temperature electric heaters.

Feed to the ATR consists of the HTSR effluent plus air. The air is preheated to 1400°F before entering the combustion zone of the ATR.

1-1902
FEED TANK

1-1306
STEAM GENERATOR

1-1405
STEAM
SUPERHEATER

1-1401
HIGH TEMPERATURE
STEAM REFORMER

1-2501
AUTOTHERMAL
REFORMER

1-1301
FIRST SH
FEED COO

1-1404
AIR PREHEATER

1-1313
HTSR/ATR EFFL.
EXCHANGER

1-1306    FC

CITY WATER

3   PI   TI-1           4

1-1405

2

FI   TI-9

Pdl        TR        9   TI-19        12

1-2501

ELECT.        ELECT.        TI-12
THRU
TI-15                    SC

TI-2
THRU
TI-8                                   10

6                    SC        TI-17   TI-10

1-1401

PI        13

1-1902        SC        1-1313        16        STEAM        1-1

TI-18        1-1

1-1404        TI

PI        BFW

TI

F-IC        TI

SC        FI                PI

1-1501   M                PI        M

PI        1-1803

FUEL   1-1504   M

1-1504
FUEL TRANSFER PUMP

1-1501
FUEL FEED PUMP

1-1803
PROCESS AIR COMPRESSOR

PCD/6629

| 1-2501 | 1-1301 | 1-2502 | 1-2503 | 1-2504 | 1-1201 |
|---|---|---|---|---|---|
| TOTHERMAL REFORMER | FIRST SHIFT FEED COOLER | FIRST STAGE SHIFT REACTOR | SECOND STAGE SHIFT REACTOR | DESULFURIZER | EFFLUENT SEPARATOR |

| 1-1313 | 1-1204 | 1-1302 | 1-1303 |
|---|---|---|---|
| HTSR/ATR EFFL. EXCHANGER | K.O. DRUM | SECOND SHIFT FEED COOLER | EFFLUENT COOLER |

LEGEND:
PI  - PRESSURE INDICATOR
TI  - TEMPERATURE INDICATOR
FI  - FLOW INDICATOR
TR  - TEMPERATURE RECORDER
PC  - PRESSURE CONTROL
FC  - FLOW CONTROL
FrIC - FLOW RATIO INDICATOR CONTROL
FQ  - FLOW SUMMATION
SC  - SAMPLE CONNECTION
BFW - BOILER FEEDWATER

Figure 1.  Process flow diagram.
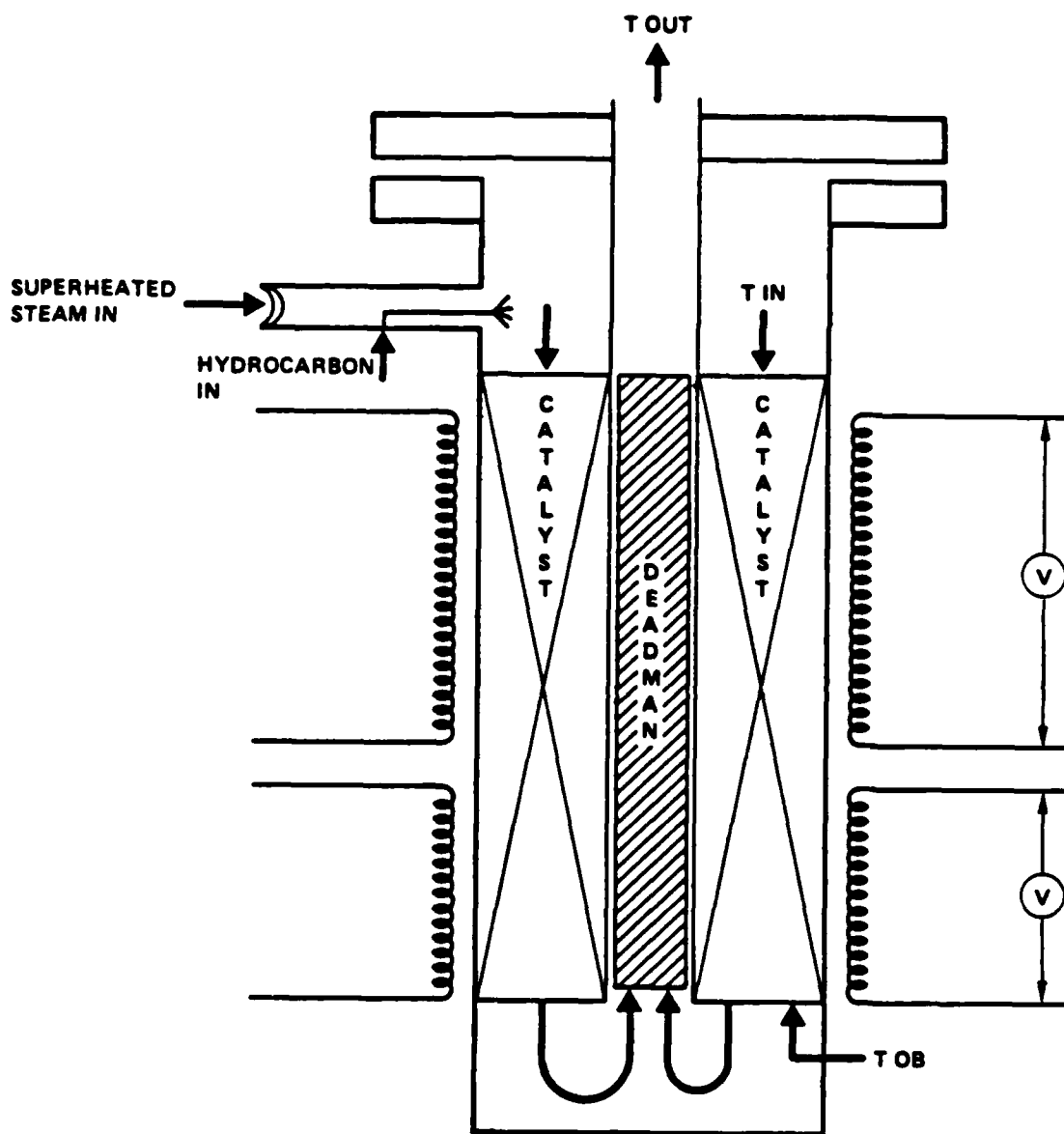
LEGEND:  T IN  = INLET TEMPERATURE OF STEAM/HYDROCARBON TO CATALYST BED

T OB = CATALYST BED OUTLET TEMPERATURE

T OUT = HTSR EXIT TEMPERATURE

Figure 2.  Sketch high temperature steam reformer (HTSR) reactor.

TABLE 1.   2 mole/hr Demonstration Plant (DP) Heat and Material Balance.
100% Capacity Operation

| STREAM NUMBER | 1 | 3 | 4 | 5 | 6 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|
| STREAM NAME | FDSTK-L | COLDSTM | HOTSTM | HTSRFD | HTSREFF | HTSRTRNS | ATRFDH | ATRAIRC |
| H2 | 0.00 | 0.00 | 0.00 | 0.00 | 7747.84 | 7747.84 | 7747.84 | 0.00 |
| N2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 7943.63 |
| CO | 0.000 | 0.000 | 0.000 | 0.000 | 1969.19 | 1969.19 | 1969.19 | 0.00 |
| A | 0.000 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 | 94.78 |
| O2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 | 2130.69 |
| C1- | 0.000 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 |
| CC2- | 0.000 | 0.000 | 0.000 | 0.000 | 3709.08 | 3709.08 | 3709.08 | 0.00 |
| CC2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 |
| CO2 | 0.000 | 0.000 | 0.000 | 0.000 | 2721.63 | 2721.63 | 2721.63 | 0.00 |
| H2S | 0.000 | 0.000 | 0.000 | 0.000 | 25.32 | 25.32 | 25.32 | 0.00 |
| CCS | 0.000 | 0.000 | 0.000 | 0.000 | 0.31 | 0.31 | 0.31 | 0.00 |
| SO2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 | 0.00 | 532.54 |
| H2O(V) | 0.000 | 24924.53 | 24924.63 | 24924.63 | 17511.80 | 17511.80 | 17511.80 | 532.54 |
| BZ---(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| JP---(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DF---A(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| OF--2(V) | 0.000 | 0.000 | 0.000 | 559.43 | 0.000 | 0.000 | 0.000 | 5895.75 |
| H2O(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| BZ---(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| JP---(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| OF--A(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DF--2(L) | 559.43 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ASH | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | | | 0.00 |
| TOTAL[a] | 559.427 | 24924.633 | 24924.633 | 25484.059 | 33685.152 | 33685.152 | 33685.152 | 16597.101 |
| PSIA[b] | 14.696 | 164.700 | 164.700 | 89.700 | 84.700 | 79.700 | 74.700 | 74.700 |
| OF[c] | 80.000 | 365.852 | 1300.000 | 969.523 | 1800.000 | 1400.000 | 1652.000 | 150.000 |
| MMBTU/HR[d] | -83.318 | -2543.072 | -2326.776 | -2410.094 | -1948.846 | -2092.424 | -2003.040 | -767.157 |

a Flow rates are in pound moles per hour (lb mole/hr) x $10^4$.
b Operating pressures are in pounds per square inch absolute (psia).
c Operating temperatures are in degrees fahrenheit (°F).
d Enthalpies are in million British thermal units per hour (Btu/hr). Enthalpy shown includes heat of reactions. Reference temperature is 77°F.

TABLE 1. 2 mole/hr Demonstration Plant (DP) Heat and Material Balance (Contd).
100% Capacity Operation

| STREAM NUMBER | ⟨12⟩ | ⟨13⟩ | ⟨16⟩ | ⟨17⟩ | ⟨18⟩ | ⟨19⟩ | ⟨20⟩ | ⟨27⟩ |
|---|---|---|---|---|---|---|---|---|
| STREAM NAME | ATPAIRH | ATREFF | ATREFFHX | 1SHFTIN | 1SHFTOUT | 2SHFTIN | 2SHFTOUT | CLEANH2 |
| $H_2$ | 0.00 | 15902.50 | 15902.50 | 15902.50 | 19531.39 | 19531.39 | 19999.87 | 19999.87 |
| $N_2$ | 7943.63 | 7943.63 | 7943.63 | 7943.63 | 7943.63 | 7943.63 | 7943.63 | 7943.63 |
| CO | 0.000 | 4411.80 | 4411.80 | 4411.80 | 632.77 | 632.77 | 212.29 | 212.29 |
| A | 94.98 | 94.98 | 94.98 | 94.98 | 94.98 | 94.98 | 94.98 | 94.98 |
| $O_2$ | 2130.67 | 0.00 | 0.00 | 0.000 | 0.000 | 0.000 | 0.00 | 0.00 |
| CO--1 | 0.000 | 19.40 | 19.40 | 19.40 | 19.40 | 19.40 | 19.40 | 19.40 |
| CO2-- | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| CO2S | 0.000 | 3968.64 | 3968.64 | 3968.64 | 7747.74 | 7747.74 | 8164.66 | 8164.66 |
| H2S | 0.000 | 25.29 | 25.29 | 25.29 | 25.57 | 25.57 | 25.002 | 25.002 |
| SO2 | 0.000 | 0.34 | 0.34 | 0.34 | 25.005 | 25.005 | 0.000 | 0.000 |
| $H_2O(V)$ | 6427.00 | 23264.31 | 23264.31 | 23264.31 | 19484.36 | 19484.36 | 19060.96 | 19060.96 |
| BZ--(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| JP--4(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DF--2(V) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $H_2O(L)$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| BZ--(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| JP--4(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| DF--2(L) | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| ASH | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| TOTAL[a] | 16597.191 | 55530.887 | 55530.887 | 55530.887 | 55530.387 | 55530.387 | 55521.406 | 55495.363 |
| PSIA[b] | 134.700 | 64.700 | 59.700 | 54.700 | 44.700 | 39.700 | 29.700 | 24.700 |
| DFC[c] | 1409.030 | 1800.544 | 1628.336 | 550.000 | 689.625 | 500.020 | 515.518 | 515.518 |
| MMBTU/HR[d] | -493.763 | -2496.802 | -2506.187 | -3100.291 | -3100.291 | -3186.420 | -3186.420 | -3185.349 |

[a] Flow rates are in pound moles per hour (lb mole/hr) x $10^4$.
[b] Operating pressures are in pounds per square inch absolute (psia).
[c] Operating temperatures are in degrees fahrenheit (°F).
[d] Enthalpies are in million British thermal units per hour (Btu/hr). Enthalpy shown includes heat of reactions. Reference temperature is 77°F.

TABLE 2.  Catalyst Characteristics.

| Service | HTSR | ATR | 1st Shift | 2nd Shift | Desulfurizer |
|---|---|---|---|---|---|
| Manufacturer | TEC[1] | TEC | United[2] | United | United |
| Designation | T-12 | T-48 | C25-2-02 | C25-2-02 | G-72D |
| Shape | Sphere | Sphere | Extrusion | Extrusicn | Pellets |
| Size, in. | 3/16 | 3/16 | 1/8 | 1/8 | 3/16 |
| Bulk Density, lb/ft$^3$ | 81 | 88 | 42 | 42 | 70 |
| Composition | Proprietary | Proprietary | Alumina Carbon monoxide Molybdenum oxide | Alumina Carbon monoxide Molybdenum oxide | Zinc oxide |

[1]Toyo Engineering Corporation, Tokyo, Japan.
[2]United Catalysts Inc., Louisville, Kentucky, U.S.A.
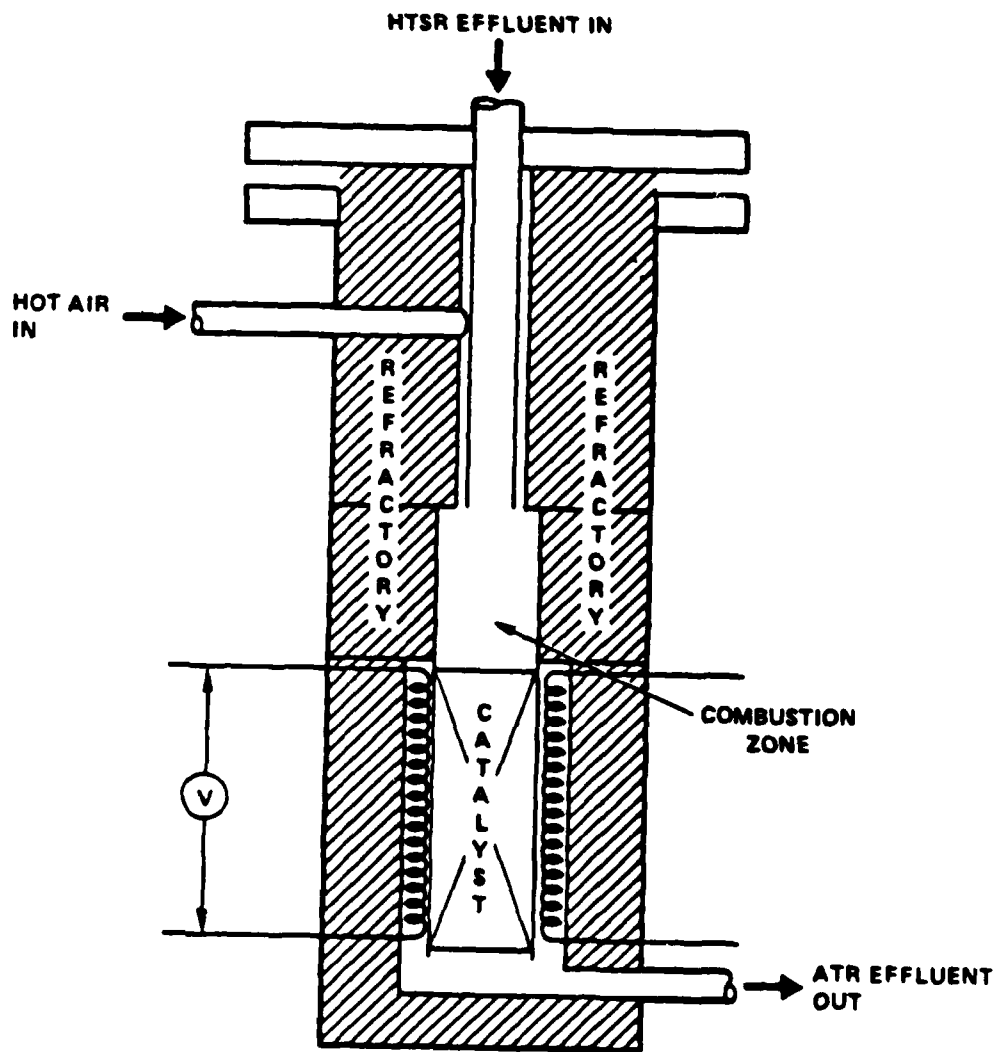
Figure 3.  Sketch, autothermal reformer (ATR) reactor.

The HTSR effluent is heat interchanged with the ATR effluent to increase the ATR feed temperature to approximately 1650°F, then combusted with preheated air. Following combustion, the reaction gases pass downward through the T-48 catalyst bed where essentially all the remaining hydrocarbons, still in the presence of steam, are converted to a mixture of hydrogen plus carbon oxides. The projected methane content in the final product is reduced to less than 0.05 mole percent.

The effluent is cooled in the feed-product interchanger, 1-1313, then further cooled to 550°F in the first shift feed cooler, 1-1301. This stream, now at approximately 55 psia, is ready for the first stage shift Reactor, 1-2502.

4. First Stage Shift Reactor

The objective of the first stage shift reactor is to increase the concentration of hydrogen by the water gas shift reaction:

$$CO + H_2O = H_2 + CO_2 \tag{1}$$

In addition to the water gas shift reaction, the cobalt-molybdenum catalyst also promotes the hydrolysis of carbonyl sulfide (COS) by the reaction:

$$COS + H_2O = H_2S + CO_2 \tag{2}$$

Feed inlet temperature is 550°F. The water gas reaction is exothermic, raising the adiabatic outlet temperature to approximately 710°F. The effluent temperature is then lowered to 500°F in the second shift feed cooler, 1-1302 to prepare it for feed to the second stage shift reactor, 1-2503.

5. Second Stage Shift Reactor

The objective of this conversion is to further increase the hydrogen concentration through the water gas shift reaction and reduce the carbon monoxide to a level acceptable as feed to the fuel cell.

The catalyst used in this process step is also cobalt-molybdenum based. The hydrogen concentration in the second shift outlet is increased by approximately 0.7 mole percent while the carbon monoxide concentration is reduced to less than 1.0%. The exothermic heat of the shift reaction increases the adiabatic effluent temperature to approximately 515°F. The product from the shift reactor now meets the criteria for fuel cell use with the exception of the sulfur content.

## 6.   Desulfurizer

The desulfurizer, 1-2504, reduces the sulfur concentration in the fuel cell feed stream to less than 10 ppmw. This is achieved by contacting the product gas stream with a zinc oxide bed where the hydrogen sulfide will react with the zinc oxide to form zinc sulfide and water according to the reaction:

$$H_2S + ZnO = ZnS + H_2O \tag{3}$$

The resulting desulfurization takes place at approximately 515°F. The heat effect is minor during the desulfurization because of the combination of small amounts of sulfur compound removed and low heat of reaction. The product gas, containing approximately 54.9 mole percent hydrogen, dry basis, represents the primary feed to the fuel cell anode.

## 7.   Heat Profile, Reactor Section

High hydrogen production efficiency requires effective heat interchange. Fig. 4 illustrates one combination of heat interchanges. It graphically depicts temperature levels and energy quantities for efficient energy recovery operations for ATR effluent cooling processes for an integrated 2 mol/hr fuel processor-fuel cell complex. The Fig. 4 example shows six heat interchanges as the ATR effluent is cooled from 1800°F to its 550°F entry temperature to the first stage shift reactor, giving up approximately 49,590 Btu/hr in the process.
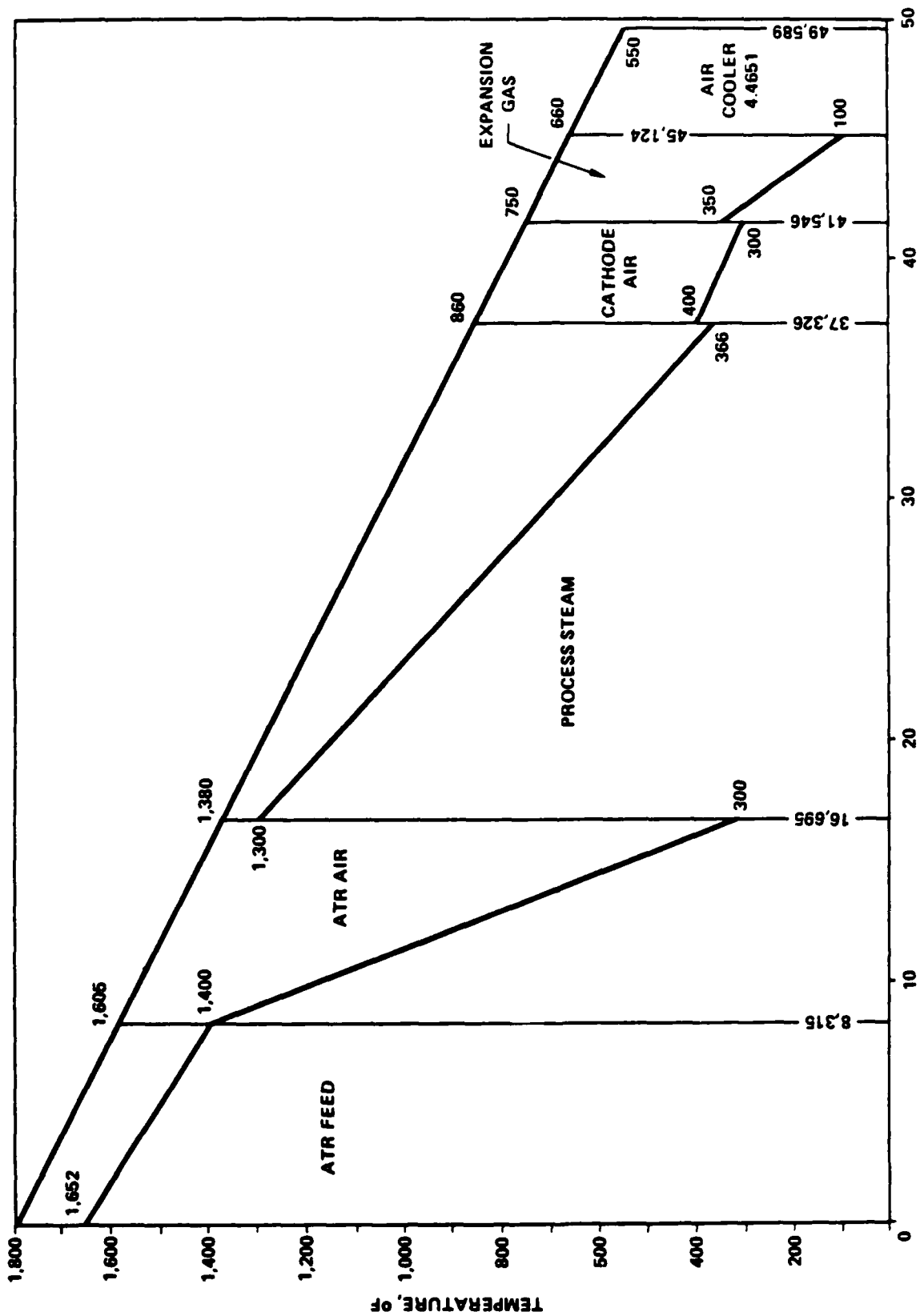
Figure 4. 2 mol/hr heat profile, reactor section.

These heat interchanges include:

| Interchange With | ATR Temperature, °F In | ATR Temperature, °F Out | Energy Receipt Stream Temperature, °F In | Energy Receipt Stream Temperature, °F Out | Energy Transferred, Btu/hr |
|---|---|---|---|---|---|
| ATR Feed Stream | 1,800 | 1,605 | 1,400 | 1,652 | 8,315 |
| ATR Air Feed Stream | 1,605 | 1,380 | 300 | 1,400 | 8,380 |
| Process Stream, Feed to HTSR | 1,380 | 860 | 366 | 1,300 | 20,631 |
| Fuel Cell and Hydrogen Recovery Streams | 860 | 660 | 100 | 400 | 7,798 |
| Heat Reject by Air Cooler | 660 | 550 | – | – | 4,465 |
| Total Heat Removed from ATR Effluent | | | | | 49,589 |

## B. HEAT AND MATERIAL BALANCE

A heat and material balance for the 2 mole/hr nominal capacity DP is shown in Table 1. The projected fuel conditioner product gas composition is:

| Component | Mole Percent, Dry Basis |
|---|---|
| Hydrogen | 54.9 |
| Carbon monoxide | 0.6 |
| Carbon dioxide | 22.4 |
| Methane | 0.1 |
| Argon | 0.3 |
| Nitrogen | 21.8 |
| Hydrogen sulfide | 1.6 ppmv |
| Carbonyl sulfide | 0.5 ppmv |
| Ammonia | 0.5 ppmv |

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# SECTION 4

## MECHANICAL DESIGN

The 2 mole/hr demonstration unit was designed to operate with a molar steam-to-carbon (s/c) ratio in the range of 3.0 to 6.0 and process conditions defined in Table 1 of Section 3. An equipment list describing the service, size/capacity, and materials of construction for the major equipment items is presented in Table 3. Location of key temperature and pressure measurements plus sample points are shown in Fig. 5. Original design space velocities and adjusted space velocities based on actual catalyst loadings for the reactors are compared in Table 4.

Materials of construction candidates for HTSR and ATR reactors, plus supporting equipment and piping, are limited because of the stream compositions (shown previously in Table 1) and the elevated design temperatures and pressures of 1600°F to 2000°F and 125 psig, respectively. Table 5 summarizes chemical compositions and Table 6 key room and elevated temperature mechanical properties of candidate alloys.

Haynes Alloy 556 and Rolled Alloy (RA) 330 were each judged to be suitable for use in both the HTSR and ATR applications. RA 330 was used because it was quickly available. Special procedures were used to qualify welders before reactor fabrication and to monitor/test the fabrication steps.

TABLE 3.  Demonstration Plant Equipment List.

| Equipment | Description | Size Capacity | Material of Construction |
|---|---|---|---|
| **Drums** | | | |
| 1-1201 | Effluent Separator | 4" ID x 4'-0" T-T | 304 SS |
| 1-1202 | Compressor Discharge Separator | 4" ID x 4'-0" T-T | 304 SS |
| 1-1204 | Knockout Drum | 12" ID x 4'-0" | 304 SS |
| **Heat Exchangers** | | | |
| 1-1301 | First Shifts Feed Cooler | 2.62 ft$^2$ | Tube - RA 330, Shell - CS |
| 1-1302 | Second Shift Feed Cooler | 0.78 ft$^2$ | Tube - CS, Shell - CS |
| 1-1303 | Effluent Cooler | 19.82 ft$^2$ | Tube - CS, Shell - CS |
| 1-1306 | Stream Generator | 100 lb/hr Steam Generation | CS |
| 1-1313 | HTSR/ATR Effluent Exchanger | 6.60 ft$^2$ | Shell - RA 330 Tube - RA 330 |
| **Heaters** | | | |
| 1-1404 | Air Preheater | 3" ID x 17'-0" Long | 316 SS |
| 1-1405 | Steam Superheater | 3" ID x 34'-0" Long | 316 SS |
| **Pumps** | | | |
| 1-1501 | Fuel Feed Pump | 2 gal/hr | API S-6 |
| 1-1504 | Fuel Transfer Pump | 1 gal/hr | API S-6 |
| **Compressors** | | | |
| 1-1803 | Process Air Compressor | 10 stdft$^3$/min | CS |
| **Tank** | | | |
| 1-1902 | Feed Tank | 1'6" ID x 3'-0" T-T | CS |

TABLE 3. Demonstration Plant Equipment List (Contd).

| Equipment | Description | Size Capacity | Material of Construction |
|---|---|---|---|
| Reactors | | | |
| 1-1401 | High Temperature Steam Reformer (HTSR) | 4.5" ID x 5'-6" T-T 1" ID Regenerative Inner Tube | RA 330 |
| 1-2501 | Autothermal Reformer (ATR) | 16" ID x 7'7" T-T | RA 330 |
| 1-2502 | First Stage Shift Reactor | 12" ID x 6'-0" T-T | 2-1/4 CR - 1 Mo |
| 1-2503 | Second Stage Shift Reactor | 12" ID x 6'-0" T-T | 2-1/4 CR - 1 Mo |
| 1-2504 | Desulfurizer | 1'-6" ID x 6'-0" T-T | CS |

Legend:  CS - Carbon Steel
304 SS - 304 Stainless Steel
RA 330 - Rolled Alloy 330: Chromium 17.0-20.0%, Nickel 34.0-37.0, Carbon 0.08% maximum, Silicon 0.75%-1.50%, Manganese 2.0% maximum, Phosphorus 0.03% maximum, Sulfur 0.030% maximum, Copper 1.0% maximum, Iron balance.

Table 4.  List of space velocities

| Equipment Number | Description | Original Design Space Velocity, $hr^{-1}$* | Design Space Velocity Per Actual Catalyst Loading, $hr^{-1}$* |
|---|---|---|---|
| 1-1401 | HTSR | 2070 | 2180 |
| 1-2501 | ATR | 6000 | 3540 |
| 1-2502 | First Stage Shift Reactor | 1000 | 490 |
| 1-2503 | Second Stage Shift Reactor | 1000 | 690 |
| 1-2504 | Desulfurizer | 165 | 210 |

*Standard cubic feet per hour of feed per cubic foot of catalyst.

1-1902
FEED TANK
18" PIPE x 3'-0" T-T
D.P. 15 PSIG
D.T. 150°F
MATERIAL: CS

1-1306
STEAM
GENERATOR
34 KW
MATERIAL: CS
NOTE 3

1-1405
STEAM
SUPERHEATER
20 KW
MATERIAL: 316SS
D.P. 150 PSIG
D.T. 1300°F

1-1401
HIGH TEMP
STEAM REFORMER
1" PIPE INSIDE
4" PIPE x 5'-6" T-T
D.P. 150 PSIG
D.T. 1820°F
26 KW
MATERIAL: RA 330

1-2501
AUTO THERMAL
REFORMER
4½" I.D. x 5'-1" T-T
D.P. 125 PSIG
D.T. 1830°F
MATERIAL: RA-330
15.6 KW

1-2502
FIRST STAGE
SHIFT REACTOR
18" PIPE x 6'-0" T-T
D.P. 125 PSIG
D.T. 735°F
MATERIAL: 28 CR 1 Mo

1-2503
SECOND STAGE
SHIFT REACTOR
12" PIPE x 6'-0" T-T
D.P. 100 PSIG
D.T. 600°F
MATERIAL: CS

1-1313
HTSR/ATR EFF.
EXCHANGER
DUTY: 13,450 BTU/HR
MAT'L SHELL: RA-330
TUBES: RA-330
D.P. 130 PSIG
D.T. 1850°F

1-1204
K.O. DRUM
12" PIPE x 4'-0" T-T
D.P. 105 PSIG
D.T. 575°F
MATERIAL: 304SS

1-1404
AIR PRE-HEATER
6.6 KW
MATERIAL: 316SS
D.P. 130 PSIG
D.T. 1490

1-1316
WASTE HEAT BOILER
DUTY: 67,540 BTU/HR
MATERIAL SHELL: CS
D.P. 75 PSIG
D.T. 310°F

CITY WATER
1"-AA-1

STEAM TRACING
TO LINE ½"-AA-8

TO GAS CHROMATOGRAPH

NITROGEN
BOTTLE

EMERGENCY
VENT

SAMPLE
COOLER

SET @
10 PSIG

VENT TO
OUTSIDE
OF BLDG.

VENT TO
OUTSIDE OF
BUILDING

SET @
150 PSIG

CATALYST
LOADING

CALIBRATION
TUBE

1-1902

DIESEL
FILTER

NO FLOW
SHUT-OFF
HEAT TO
HTSR 1-1401

RATIO
CONTROL

DEW
POINT

NITROGEN START-UP

SET @
100 PSIG

PULSATION
DAMPENER

PULSATION
DAMPENER

SET @
200 PSIG

CITY WATER

DIESEL

ATOMIZER

DETAIL 'A'

STEAM

1-1504
FUEL TRANSFER
PUMP
CAPACITY: 1 GPM
DIFF PRESS: 50 PSI
¼ HP

1-1501
FUEL FEED PUMP
CAPACITY: 2.0 GPM
DIFF PRESS: 250 PSI
¼ HP
MATERIAL: APE S-6

1-1803
PROCESS AIR COMPRESSOR
CAPACITY: 10 SCFM
DIFF PRESS: 180 PSI
5 HP
MATERIAL: CS

Figure 5. Piping and instrument diagram.

TABLE 5.  Chemical Composition of Alloys Suitable for Operating
Temperatures of 1600°F to 2000°F and Pressure of 125 psig.

| | Haynes Alloy 556 | Rolled Alloy 330 | Inconel 600 | Alloy 800 | HK-40 (Cast) | HP-Nb Mod (Cast) | Super-therm (Cast) |
|---|---|---|---|---|---|---|---|
| Carbon | 0.1 | 0.08 | 0.15 | 0.05 | 0.40 | 0.1 | 0.50 |
| Silicon | 0.4 | 1.25 | 0.5 | 0.35 | 1.50 | 1.3 | 1.20 |
| Manganese | | 2.0 | 1.0 | 0.75 | 1.50 | 1.0 | 1.20 |
| Chromium | 22.0 | 18.5 | 15.5 | 20.0 | 25.0 | 25.0 | 28.0 |
| Nickel | 20.0 | 35.5 | 72.0 | 32.0 | 20.0 | 35.0 | 35.0 |
| Cobalt | 20.0 | | | | | | |
| Tungsten | 3.0 | | | | | | 5.5 |
| Columbium and Tantalum | 0.8 | | | | | | |
| Molybdenum | 3.0 | | | | | | |
| Copper | | 1.0 | 0.5 | | | | |
| Iron | | | 8.0 | | | | |
| Aluminum and Titanium | | | | $\geq$0.7 | | | |
| Niobium | | | | | | 1.2 | |

TABLE 6.   Room and Elevated Temperature Mechanical
           Properties of Candidate Alloys.

| | Haynes Alloy 556 | Rolled Alloy 330 | Inconel 600 | Alloy 800 | HK-40 (Cast) | HP-Nb Mod (Cast) | Super-therm (Cast) |
|---|---|---|---|---|---|---|---|
| **Room Temperature:** | | | | | | | |
| Ultimate Tensile Strength | 118,000 | 85,000 | 90,000 | 80,000 | 75,000 | 66,000 | 65,000 |
| Yield Strength | 59,500 | 39,000 | 40,000 | 35,000 | | 26,000 | 36,000 |
| Percent Elongation | 47 | 47 | 45 | 35 | 16 | 20 | 3 |
| **Stress to Produce Rupture 100,000 hr (psi):** | | | | | | | |
| 1400°F | 12,800 | 2,800 | 3,800 | 4,000 | 4,500 | 4,100 | - |
| 1600°F | 5,200 | 1,000 | 1,500 | 1,600 | 2,250 | 2,600 | 3,650 |
| 1800°F | 1,900 | 310 | 730 | 620 | 875 | 1,200 | 1,600 |
| 2000°F | | - | 400 | - | 290 | 650 | 610 |
| **Notes:** | 10,000 hr | | Hot Rolled Annealed | | | | |

SECTION 5

RELIABILITY ANALYSIS

A. INTRODUCTION

Preliminary reliability analyses were conducted in parallel with the detailed
DP design development. These analyses investigated critical areas for the
demonstration plant (DP) and estimated the mean time between failure (MTBF),
the mean time to repair (MTTR), and the inherent availability (Ai) of the
system. The results are summarized below.

Relevant Studies included:

(1) Preliminary hazards analysis (PHA). To identify appropriate design
criteria for safety areas.

(2) Reliability assessment. To estimate the systems MTBF.

(3) Maintainability assessment. To estimate the MTTR.

(4) Availability calculation. To estimate the systems Ai to produce a
hydrogen-rich gas.

B. PRELIMINARY HAZARDS ANALYSIS

The PHA, defined by MIL-STD-882B, was performed to obtain an initial risk
assessment of the DP. Its purpose was to assess the risk for each identified
potential hazard. The PHA was performed early in the program so that the
safety considerations could be included in the design criteria.

C. RELIABILITY ASSESSMENT, 2 MOLE/HR DEMONSTRATION PLANT

The piping and instrument diagram (P&ID) for the DP was used to identify the
single point failures for the items that are essential for the unit's

operation. The PHA worksheets for the 13 subsystems described in the PHA are included in Appendix A. The worksheets list single point failures. Instrument and controls used only for analytical functions were not included in single point failure listing. The analysis result indicated a MTBF of 4,471 hr or two failures per year.

Individual items, their failure rate, MTTR, and data source reference are listed in Table 7. Data sources are presented in the list of references located at the end of this section.

D. MAINTAINABILITY ASSESSMENT

The MTTR for unscheduled failure was estimated to be 2.3 hr per event, or about 5 hr/yr. Scheduled maintenance is estimated to be 6 hr/mo or 72 hr/yr, which is a 99.18% availability factor.

E. AVAILABILITY CALCULATION

The Ai of the DP is obtained by the following equation:

$$Ai = \frac{MTBF}{MTBF + MTTR} \qquad (4)$$

The preliminary estimate for Ai is 99.95%. Including scheduled downtime the estimated availability is 99.13%.

F. RELIABILITY ANALYSIS, 20 MOLE/HR FUEL CONDITIONER

A 20 lb mole fuel processor process flow diagram was compared with the DP P&ID. It was concluded that the DP failure modes and effects analysis (FMEA) performed for the PHA and the reliability, maintainability, and availability (RAM) analyses for the DP are useful as predictors for the performance of the 20 mole/hr facility.

TABLE 7. Reliability Analysis Summary.

| Tag No. | Item | Quantity | Failure Rate $\times 10^{-6}$* | MTTR | Reference (see subsection G) |
|---|---|---|---|---|---|
| 1-1306 | Steam Generator | 1 | 19.200 | 4 | 1 |
| 1-1405 | Steam Superheater | 1 | 0.400 | 4 | 1 |
| 1-1401 | HTSR Heater | 1 | 2.290 | 8 | 1 |
| 1-2501 | ATR Heater | 1 | 2.290 | 8 | 1 |
| 1-1501 | Fuel Feed Pump | 1 | 50.000 | 2 | 2 |
| 1-1803 | Process Air Compressor | 1 | 9.510 | 2 | 1 |
| 1-1404 | Air Heater | 1 | 2.290 | 2 | · 1 |
| FV-1,-2, -5 | Flow Elements | 3 | 7.938 | 2 | 2 |
| | Flow Transmitter | 1 | 7.800 | 2 | 2 |
| | Flow Indicator | 1 | 7.938 | 2 | 2 |
| | Flow Switch Low | 1 | 7.800 | 2 | 2 |
| | Flow Alarm Low | 1 | 1.500 | 2 | 2 |
| | Flow Valve Air OP | 3 | 2.464 | 2 | 2 |
| | Flow Recorder Controller | 1 | 9.891 | 2 | 2 |
| | Flow Indicator Controller (Ratio) | 1 | 10.147 | 2 | 3 |
| HV-1 | Three-way Solenoid | 1 | 1.640 | 2 | 5 |
| | Hand Switch | 1 | 2.710 | 2 | 4 |
| | Temperature Transmitter | 1 | 3.617 | 2 | 3 |
| | Temperature Switch High/Low | 2 | 2.511 | 2 | 2 |
| | Temperature Alarm Low | 1 | 1.500 | 2 | 1 |
| PSV-1, -2, -3 | Pressure Safety Valve | 3 | 2.517 | 2 | 1 |
| PCV-18 | Pressure Control Valve | 1 | 4.928 | 2 | 2 |
| | Flow Quantity Indicator | 1 | 7.938 | 2 | 2 |
| 1301, 1302, 1303A | Cooler | 3 | 0.900 | 2 | 4 |
| | | 83 | 223.682 | | |

MTBF = 4471 hr
MTTR = 2.3 hr
Ai = 0.9995

*$\times 10^{-6}$ = the number of failures expected to occur in one million hours of operation.

The predicted MTBF for the 20 mol/hr plant is projected to be at least two failures per year. The MTTR is 2.3 hr for random failures. The predicted Ai is 99.95%. Including scheduled downtime of 72 hr/yr, the estimated availability is 99.13%.

For a larger plant capacity we anticipate that electrical heating of the HTSR and ATR will be replaced by direct fired heating. Experience and judgment indicate that the reliability of the direct fired heaters will be equal to, or greater than, electrical heaters.

G. REFERENCES

References noted on Table 7 are listed below:

(1) Nonelectronic Parts Reliability Data, Reliability Analysis Center, Rome Air Development Center, Summer 1978.

(2) Reliability/Availability Analysis for Process Equipment Design, Munitions Production Base Modernization and Expansion, RDX/HMX Expansion Facility, DRC Project No. 5XX2668, The Ralph M. Parsons Company, October 1979.

(3) Parsons Job No. 3966-100, Safeguard Reliability Data Collection.

(4) GIDEP Failure Data Interchange, Vol. 1, 1975, Vol. 2, 1976.

(5) "Nuclear Plant Reliability Data System," Annual Report, Cumulative System and Component Reliability, NUREG/CR-1635, Prepared for American Public Power Association, Edison Electric Institute, Tennessee Valley Authority, and U.S. Nuclear Regulatory Commission by Southwest Research Institute, 1979.

SECTION 6

DEMONSTRATION PLANT CONSTRUCTION/COMMISSIONING

A.  DETAILED ENGINEERING

Detailed engineering proceeded at a moderate pace during the preliminary
demonstration plant (DP) design review cycle. Its pace quickened significantly
following authorization to proceed with DP detailed design, procurement, and
construction.

The Fig. 5 (in Section 4) shows the DP as constructed and operated. The
project was schedule-driven with procurement schedules dictating equipment,
controls, and materials selection in many instances.

B.  PROCUREMENT

Procurement activity accelerated coincident with authorization to construct
the DP and peaked 9 weeks later. Seventy purchase orders were generated and
processed resulting in 260 material shipment receipts.

The usual procurement objective was equipment receipt in 2 to 4 weeks. Most
initial vendor bids cited significantly longer delivery times. To compress the
project schedule, corrective actions were taken including investigation and
selection of alternative equipment, materials, and vendors.

C.  FACILITIES PREPARATION

Plans for preparation of the DP operating area were formulated early. This
included acquisition of permit approvals, utilities supply, acquisition of
construction tools, and modification of the operating room to conform to fire
and explosion-proof codes.

D. CONSTRUCTION/COMMISSIONING

Construction move-in was the third week following authorization to proceed.
The DP was mechanically complete in 16 weeks. DP equipment commissioning began
during the twelfth week and was completed at the end of the sixteenth week.

Photographs of the DP are shown in Fig. 6, Fig. 7, and Fig. 8.



Figure 6.   Photograph of demonstration plant (view A).
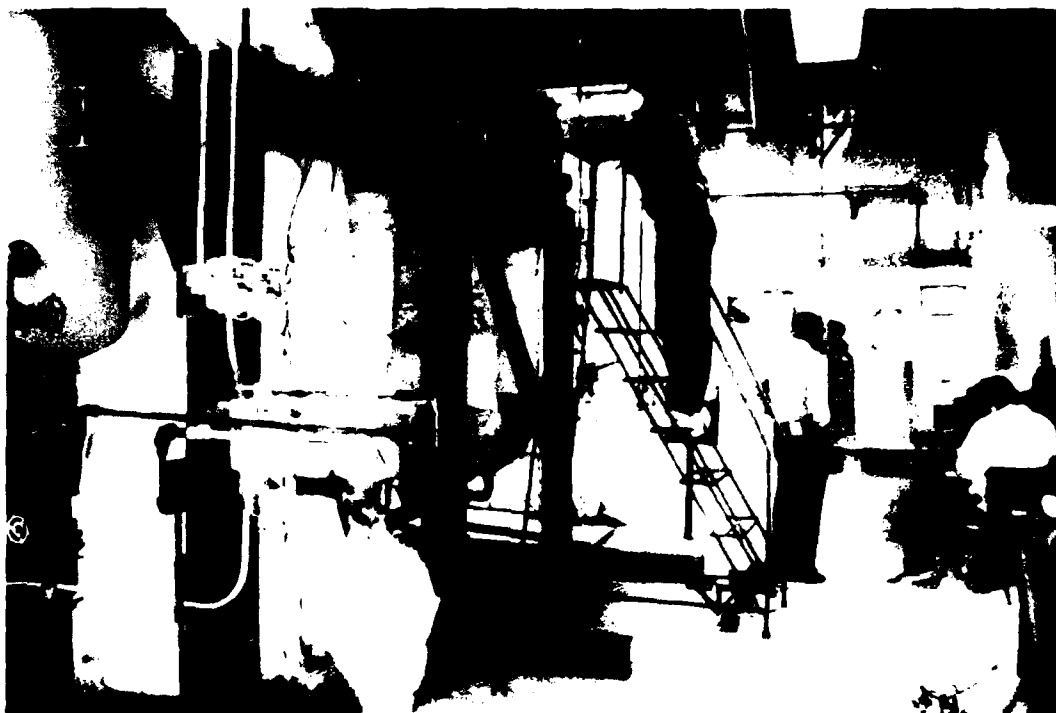
Figure 7. Photograph of demonstration plant (view B).
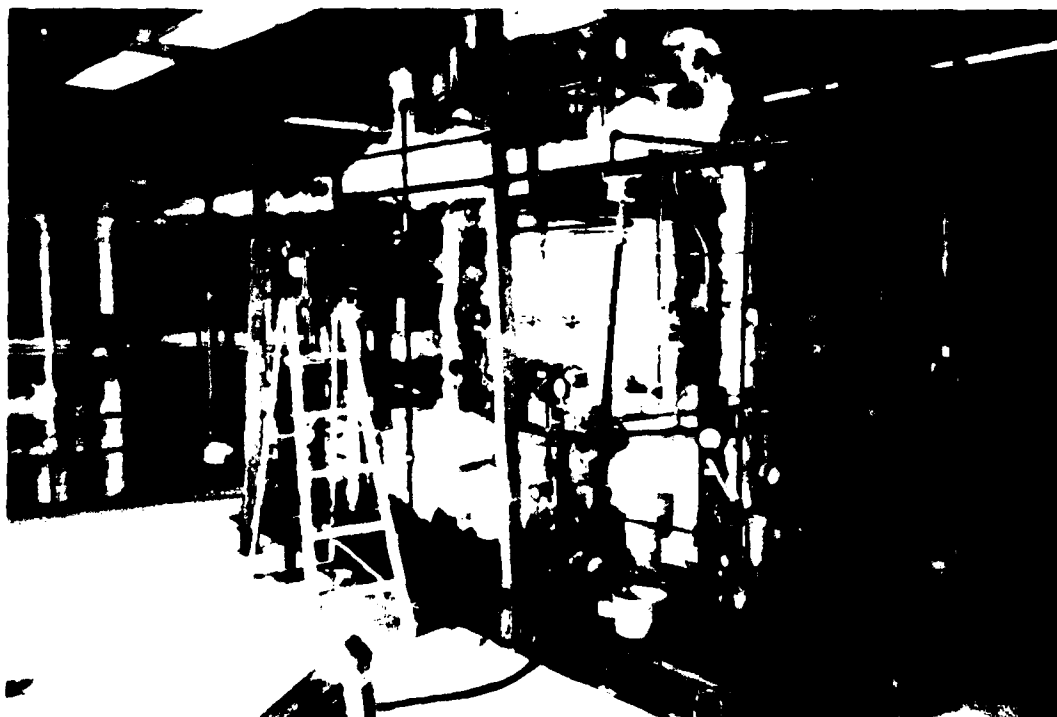


Figure 8. Photograph of demonstration plant (view C).

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SECTION 7

OPERATIONS PLAN

A.  OPERATING MANUAL

An operating manual was prepared for internal operator training, plant
commissioning, and operations use. This manual defined the process
configuration, instructions for plant commissioning, and procedures for
startup, steady-state operations, transient operations, data
procurement/recording, and shutdown. An illustrative excerpt from this manual
is included as Appendix B.

B.  OPERATIONS/TEST PLAN

The objective was to complete a 400-hr demonstration run. During the course of
this demonstration period the plan included steady-state operating periods
plus subjecting the demonstration plant (DP) to rapid startups, rapid
transient periods to simulate quick load changes in a fuel cell power plant,
and multiple shutdowns/startups. Key elements of the demonstration program
test plan are described in the following paragraphs.

1.  Cold Starts

The objective of the cold start operations was to investigate the effect
of frequent and rapid heatups on the catalysts T-12 and T-48. The experimental
results would provide information concerning the integrity and activity
degradation of the catalysts.

2.  Hot Starts

The objective of the hot start operations was to investigate the effect of
frequent and rapid heatups from a hot standby condition on catalysts T-12 and
T-48 and the DP system. The experimental results would provide information

concerning system performance under conditions simulating required response of a Remote Site Fuel Cell Power Plant.

### 3. Operations

The objective of the program operation was to demonstrate the steady-state ability of the process to produce a hydrogen-rich gaseous product from hydrocarbon liquids fuel suitable for use in a phosphoric acid fuel cell (PAFC).

### 4. Transients

The objective of transient operations was to demonstrate load-following response capability of the system; also, the effect of transients on performance, reliability, and operability of the system.

## C. PROGRAM OPERATION SCHEDULE

The program operation schedule comprised four groups of experiments consisting of experiments A, B, C, and D. These planned experiments incorporated the cold starts, hot starts, transients, and steady-state operations discussed above. The schedule was 4 weeks duration.

The demonstration experiment schedules are depicted in Tables 8, 9, and 10. The test runs were designed to demonstrate that the proposed process is capable of consistently producing a hydrogen-rich gaseous product suitable for use as a feed to a PAFC from liquid fuel and to produce data to quantitatively confirm the ability to produce 0.365 lb of hydrogen per pound of fuel consumed. They consisted of one 264-hour continuous run spanning a period of 12 days followed by ten 16-hr duration runs to be completed over a period of 2 weeks. During the course of the scheduled 400-plus hours operation, the plan included three cold startups and eight cold (overnight) startups from intermediate temperatures.

TABLE 8. Demonstration Run, Experiment A.

| Time/Day | M | T | W | T | F | S | S | M | T | W | T | F |
|----------|---|---|---|---|---|---|---|---|---|---|---|---|
| 8:00 a.m. | o | | | | | | | | | | | |
| 9:00 | o | | | | | | | | | | | |
| 10:00 | o | | | | | | | | | | | |
| 11:00 | o | | | | | | | | | | | |
| 12 noon | o | | | | | | | | | | | |
| 1:00 p.m. | o | | | | | | | | | | | |
| 2:00 | o | | | | | | | | | | | |
| 3:00 | o | | | | | | | | | | | |
| 4:00 | o | | | | | | | | | | | |
| 5:00 | o | | | | | | | | | | | |
| 6:00 | o | | | | | | | | | | | |
| 7:00 | o | | | | | | | | | | | |
| 8:00 | o | | | | | | | | | | | |
| 9:00 | o | | | | | | | | | | | |
| 10:00 | o | | | | | | | | | | | |
| 11:00 | o | | | | | | | | | | | |
| 12:00 | o | | | | | | | | | | | |
| 1:00 a.m. | o | | | | | | | | | | | |
| 2:00 | o | | | | | | | | | | | |
| 3:00 | | | | | | | | | | | | x |
| 4:00 | | | | | | | | | | | | x |
| 5:00 | | | | | | | | | | | | x |
| 6:00 | | | | | | | | | | | | x |
| 7:00 | | | | | | | | | | | | x |
| 8:00 | | | | | | | | | | | | x |

Total Operation Hours: 264

o = Cold Startup 18 to 24 hours
— = Normal Operation 264 hours
x = Shutdown and place unit in cold standby 2 to 3 hours

TABLE 9. Demonstration Run, Experiment B, Series I.

| Time/Day | Mon | Tue | Wed | Thur | Fri |
|---|---|---|---|---|---|
| | | | Series I | | |
| 8:00 a.m. | ◊ | + | + | + | + |
| 9:00 | ◊ | + | + | + | + |
| 10:00 | ◊ | + | + | + | + |
| 11:00 | ◊ | + | + | + | + |
| 12 noon | ◊ | | | | |
| 1:00 p.m. | ◊ | | | | |
| 2:00 | ◊ | | | | |
| 3:00 | ◊ | | | | |
| 4:00 | | | | | |
| 5:00 | | | | | |
| 6:00 | | | | | |
| 7:00 | | | | | |
| 8:00 | | | | | |
| 9:00 | | | | | |
| 10:00 | | | | | |
| 11:00 | | | | | |
| 12:00 | | | | | |
| 1:00 a.m. | o | o | o | o | x |
| 2:00 | o | o | o | o | x |
| 3:00 | o | o | o | o | x |
| 4:00 | o | o | o | o | x |
| 5:00 | o | o | o | o | x |
| 6:00 | o | o | o | o | x |
| 7:00 | o | o | o | o | x |
| 8:00 | o | o | o | o | x |

Total Operation Hours: 80

◊ = Quick Cold Startup - 8 hours
— = Normal Operation - Total 60 hours
+ = Hot Startup 3 Hours - Total 12 hours
o = Shutdown - Place Unit in Cold (overnight) Standby
x = Shutdown - Place Unit in Cold Standby

TABLE 10.  Demonstration Run, Experiment B, Series II, C and D.

| Time/Day | Mon | Tue | Wed | Thur | Fri |
|---|---|---|---|---|---|
| | Exper. B, Series II | | | Exper. C | Exper. D |
| 8:00 a.m. | ◊ | + | + | + | + |
| 9:00 | ◊ | + | + | + | + |
| 10:00 | ◊ | + | + | + | + |
| 11:00 | ◊ | + | + | + | + |
| 12 noon | ◊ | \| | \| | \| | \| |
| 1:00 p.m. | ◊ | | | | |
| 2:00 | ◊ | | | | |
| 3:00 | ◊ | | | | |
| 4:00 | \| | | | | |
| 5:00 | | | | | |
| 6:00 | | | | | |
| 7:00 | | | | | |
| 8:00 | | | | | |
| 9:00 | | | | | |
| 10:00 | | | | | |
| 11:00 | | | | | |
| 12:00 | | | | | |
| 1:00 a.m. | o | o | o | c | x |
| 2:00 | o | o | o | o | x |
| 3:00 | o | o | o | o | x |
| 4:00 | o | o | o | o | x |
| 5:00 | o | o | o | o | x |
| 6:00 | o | o | o | o | x |
| 7:00 | o | o | o | o | x |
| 8:00 | o | o | o | o | x |

Total Operation Hours: 80

◊ = Quick Cold Startup - 8 hours
— = Normal Operation - Total 60 hours
+ = Hot Startup 3 Hours - Total 12 hours
o = Shutdown - Place Unit in Cold (overnight) Standby
x = Shutdown - Place Unit in Cold Standby

D.  PLANNED TEST DATA COLLECTION FREQUENCY

Data collection procedures included:

(1)  Operating temperature and pressure profiles to be monitored
     continuously and recorded at 30-min intervals.

(2)  High temperature steam reformer (HTSR), autothermal reformer (ATR),
     and desulfurizer gas effluent compositions to be analyzed once every
     hour by gas chromatograph.

(3)  Total hydrocarbon and hydrocarbons heavier than methane in the HTSR
     effluent to be analyzed once a day.

(4)  Ammonia content in the ATR effluent to be analyzed once a week.

(5)  Steam-to-carbon ratio to be checked by dew point measurement of HTSR
     and ATR effluents at 30-min intervals.

(6)  First and second stage shift reactor effluent gas compositions to be
     analyzed every 4 hr.

(7)  Feed process water compositions to be analyzed once a week.

(8)  Two representative samples of the DF-2 feedstock to be analyzed. All
     DF-2 feed to be drawn from a common supply source.

(9)  DF-2 and steam feed rates to be monitored continuously and recorded
     at 30-min intervals.

(10)  Product gas flow rate and cumulative quantity of gas produced to be
      recorded at 30-min intervals.

E. ANALYTICAL PROCEDURES

1. Gas Analysis

Gas chromatographic techniques were used to analyze compositions of gas samples extracted from key locations in the DP. A Tracor Model 540 gas chromatograph was used, which consists of two analytical columns. A Carbosieve S-II column separates the gas components. A thermal conductivity detector was used to identify and quantify hydrogen, carbon monoxide, carbon dioxide, nitrogen, and methane. A Supelpak-S column separates the gas components and a flame ionization detector (FID) was used to identify and quantify hydrogen sulfide and carbonyl sulfide. The HTSR effluent was analyzed for total hydrocarbon content once per day using infrared spectrometry. Simultaneously, hydrocarbons heavier than methane in the HTSR effluent were analyzed by a second gas chromatograph with a Carbosieve S-II column. Ammonia content in the ATR effluent was analyzed once a week by bubbling the ATR effluent gas sample through a boric acid solution and determining the ammonia concentration by titration with 0.1N hydrochloric acid.

To speed up the analytical process, temperature programming techniques were used to control the velocity with which the separate gas components traverse the analytical columns. For a typical gas component, column traverse speed and time span is temperature dependent. The retention time of a gas component was controlled by manipulating the column temperature. By computer programming designated column temperatures at predetermined time spans over the entire gas spectrum, the different gas components can be identified and quantified in a timely and controlled fashion.

Moisture content of the HTSR and ATR effluent gases were analyzed once a day by a condensation method established as EPA Method 5 to confirm locally mounted dew point measurements by operating personnel.

## 2. Water Analysis

Analytical methods and procedures described in "Standard Methods for the Examination of Water and Wastewater" 16th Edition 1985, published by American Public Health Association, APHA-AWNA-WPCF, were used for analyzing process water.

Tustin, California tap water was used to feed the DP steam generator, 1-1306. The water analysis consists of total solids, total suspended solids, total dissolved solids, iron, lead, tin, chlorine, bromine, fluorine, iodine, sulfur, bacteria count, bacteria type, and electrical resistance.

## 3. DF-2 Analysis

ASTM Standard methods as specified by Military Specification MIL-F-16884G, 7 March 1973, were used to analyze DF-2:

| Test | ASTM Methods |
|------|--------------|
| Flash Point | D 93 |
| Cloud Point | D 2500 |
| Specific Gravity | D 287 |
| Pour Point | D 97 |
| Water and Sediment | D 2709 |
| Carbon Residue | D 524 |
| Ash | D 482 |
| Distillation Temperature | D 86 |
| Viscosity | D 445 |
| Sulfur | D 129 |
| Copper Corrosion | D 130 |
| Cetane Number | D 976 |
| Accelerated Stability | D 2274 |
| Neutralization | D 974 |
| Aniline Point | D 611 |
| Ignition Quality | D 613 |

SECTION 8

STARTUP AND OPERATIONS RESULTS

A. CATALYST PREPARATION

Toyo Engineering Corporation's (TEC's) T-12 catalyst was used in the high
temperature steam reformer (HTSR) and TEC's T-48, augmented by a small amount
of T-12, was used in the autothermal reformer (ATR). These catalysts are
introduced to the reactors in their oxidized state and prepared in situ for
operations service using procedures similar to those used for conventional
steam reforming catalysts, such as contact with a mixture of nitrogen ($N_2$),
hydrogen ($H_2$), and hydrogen sulfide ($H_2S$). However, for this test program,
DF-2, air, and steam were fed to the reformers to produce the $H_2$ and $H_2S$ in
situ in recognition that $N_2$, $H_2$, and $H_2S$ may not be available for startup of
fuel conditioners at remote sites.

Thiophene was added to the purchased DF-2 to bring the sulfur content to 0.5%
by weight, approximately 70% of the maximum allowable level under the
pertinent specifications VV-F 800C, MIL-T-5624-L.

United Catalysts Corporation's cobalt-molybdenum (CoMo) based catalysts were
used in the first and second stage shift reactors (1-2502 and 1-2503). These
catalysts must be activated by being presulfided and reduced.

The refractory lining of the ATR was dried and cured in place before being
exposed to higher operating temperatures. The HTSR catalyst and the ATR,
including refractory and catalyst bed, were heated to 250°F at a rate of
30°F/hr. They were then held at 250°F for 10 hr, then heated at a rate of
50°F/hr to 500°F where they were held for 8 hr. The HTSR and ATR catalysts
were then heated at 65°F/hr to operating temperature.

The heatup process, requiring approximately 48 hr, was continued until TI-8 of
HTSR reached 1800°F, TI-14 of ATR reached 1600°F, TI-20 of the first stage

shift reactor reached 460°F, and TI-21 of the second stage shift reactor reached 470°F. The catalysts were then ready for reduction and presulfidation.

In situ generation of the reducing and presulfiding gases was begun by injection of DF-2 into the HTSR at 25% of design flow rate. The feed DF-2 was injected into superheated steam in the feed nozzle of the HTSR and the resulting DF-2/steam vapor mixture entered the catalyst bed to be reformed to produce hydrogen, carbon monoxide, carbon dioxide, methane, hydrogen sulfide, and some light hydrocarbons.

The steam reforming reaction is endothermic while the catalyst reduction and sulfidation reactions are exothermic. An endotherm was indicated by a gradual temperature drop at the top of the HTSR catalytic bed. No exotherm temperature increases were observed in the HTSR. Heat inputs by external electrical heaters and heat loss were factors in observed temperature responses and profiles.

The HTSR product gases passed in series through the ATR, first and second shift reactors, and the desulfurizer. Temperature "spikes" occurred in the shift reactors as recorded by TI-20 and TI-21. The DF-2 feed to the HTSR was continued until gas analysis confirmed the presence of hydrogen in the desulfurizer effluent. The demonstration plant (DP) catalysts were then judged to be ready for operation.

B.  CATALYST PHYSICAL TESTS

The operations plan included rapid startups and abrupt transient conditions relative to normal hydrogen-producing catalyst use procedures. To illustrate, a normal catalyst heatup cycle may be in the range of 18 hr while the operations plan called for heatup periods of 3 to 8 hr. A series of laboratory tests were, therefore, conducted to determine the effect of rapid heating on the physical strength and integrity of the catalysts.

For the experiment, samples of T-12 and T-48 catalyst pellets were packed in 1-ft (length) vertical quartz tubes and placed in a tube furnace. Three such

packed tubes were placed in the furnace for each run. A slow gas stream was passed through the catalyst bed during the heating/cooling cycle. An air stream was passed during heating or cooling when the catalyst bed was below 800°F and dry nitrogen was above 800°F.

The heating/cooling cycle was:

    Step 1  =  1-1/2 hr from ambient to 400°F
    Step 2  =  1-1/2 hr from 400°F to 1800°F
    Step 3  =  1 hr @ 1800°F (constant temperature)
    Step 4  =  1-1/2 hr from 1800°F to 400°F
    Step 5  =  1-1/2 hr from 400°F to ambient

Three heating/cooling cycles were performed on each catalyst.

After three cycles, the catalyst pellets were removed from the quartz tubes and the pellets were examined for dusting, cracking, and other changes. Observation revealed that there was no noticeable change in the catalysts' physical appearance as a result of the cycles. No dusting or cracking was detected.

A pressure test, applied on the pellets, gave erratic results on the pellets before and after the cycling. The test could not detect a reproducible difference between the pressure at which the "before" and "after" catalyst pellets disintegrated.

The conclusion was that the T-12 and T-48 catalysts maintained their integrity during the three-cycle rapid heating/cooling cycle tests.

C.  OPERATING PROCEDURE

The reactors and vessels were heated to operating temperature and the catalysts were conditioned as described earlier. The steam feed to the HTSR was started at 60 lb/hr = 3.33 lb mole/hr. The maximum steam preheat temperature attained was 1150°F because of the maximum temperature reached in

the preheater (1-1306) and the high heat loss in the transfer line between 1-1306 and the HTSR. The design steam feed temperature to the HTSR was 1300°F.

When the steam feed rate and temperature stabilized, the DF-2 feed was started at approximately 7 lb/hr = 0.50 mole/hr of carbon resulting in a steam-to-carbon ratio (s/c) of 6.7 moles of steam per atom of carbon. Introduction of the feed to the HTSR catalyst bed resulted in temperature drops for thermocouples TI-2 through TI-7 caused by the endothermic reaction. The electrical heater controls were adjusted to bring the maximum bed temperature to 1800°F although there was a significant variation in temperature over the height of the bed, which will be defined in Fig. 9 and discussed later.

The heat required to sustain the HTSR endothermic reactions at 1800°F was estimated to be approximately 39 thousand (39 k) Btu/hr and it came from two sources.

One source was heat transfer from the nominal 1800°F catalyst bed effluent in the inner, or regenerative, tube of the HTSR to the HTSR catalyst bed. The reactor was designed to transfer adequate heat from the regenerative tube to the catalyst bed gas to reduce the inner tube gas effluent temperature to 1400°F. This heat source accounts for approximately one-third of the total endothermic reaction heat requirements. The remaining two-thirds was added by the external electrical heaters. In addition, the electrical heaters must compensate for heat loss to the surroundings, estimated to be approximately 8.6 kW or 29.4 kBtu/hr.

Measurements indicated that the HTSR effluent exiting the regenerator tube was close to its design temperature of 1400°F. TI-9, located at the 1-1313 inlet was 1260°F and the estimated heat loss through the transfer pipe from the HTSR outlet to TI-9 results in a calculated HTSR effluent temperature in the range of 1350°F to 1400°F.

The flow ratio controller FFIC-5 was bypassed for startup. The control valve FV-5 was manipulated manually to deliver air to the ATR. The air flow rate was
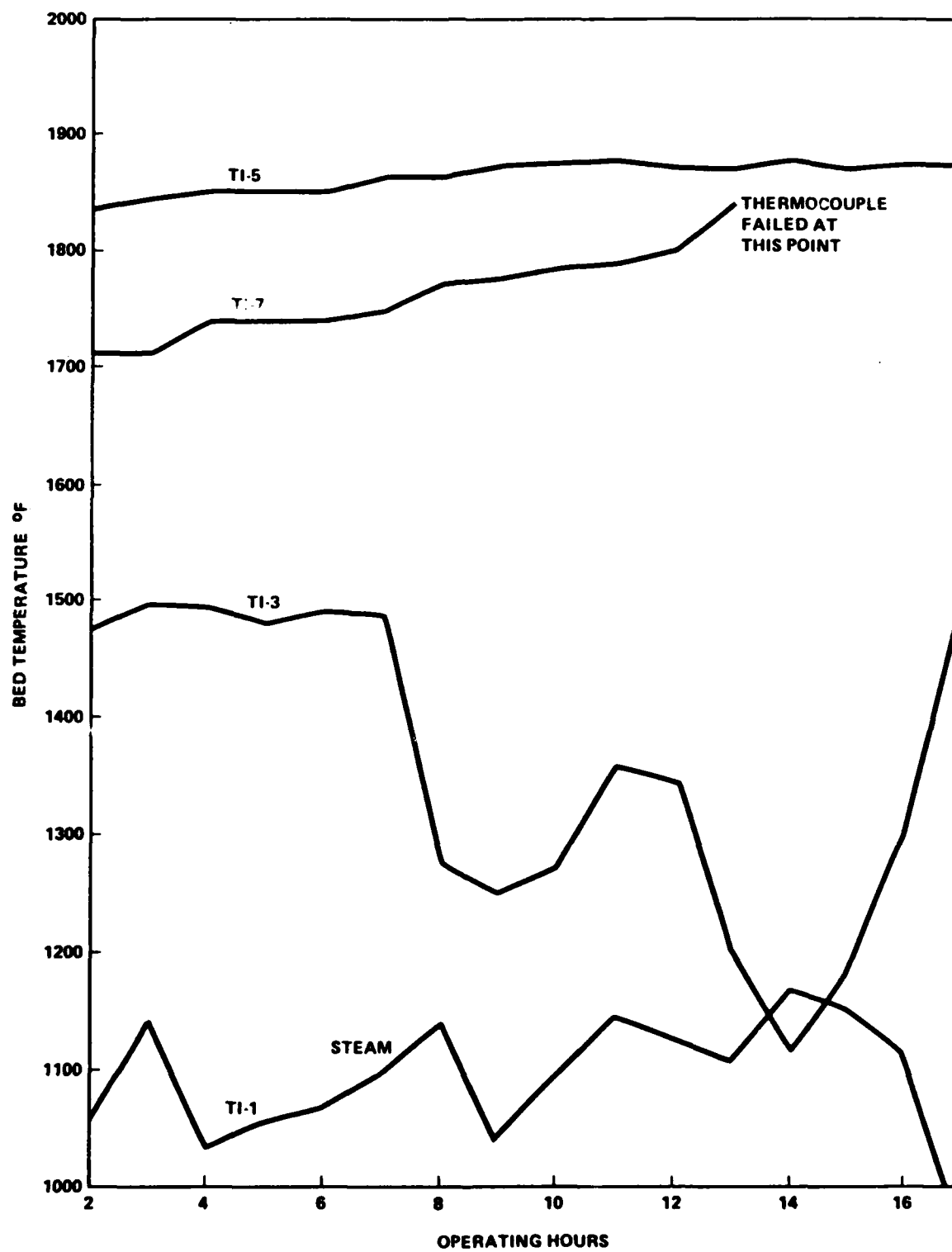
Figure 9.  HTSR operating temperature profile versus time.

set at 280 stdft$^3$/hr. Air entering the ATR was preheated to 1150°F by the air preheater, 1-1404. The design air preheat temperature of 1400°F was not achieved because of limitation in maximum temperature in 1-1404 and high heat loss in the transfer line from 1-1404 to the ATR inlet.

HTSR methane contained in the effluent was further reformed to hydrogen and carbon monoxide by partial oxidation in the ATR catalyst bed. The ATR electrical heaters were adjusted to supply heat to compensate for the heat loss to the surrounding environment by the ATR. The ATR catalyst bed temperature was maintained at above 1800°F as indicated by thermocouple TI-13 although other ATR thermocouples (TI-12, TI-14, and TI-15) indicated lower temperatures, in the range of 1500°F to 1650°F; see Fig. 10.

The ATR effluent, at 1650°F, exchanged heat with the HTSR effluent in the HTSR/ATR effluent exchanger (1-1313) and partially bypassed the first shift feed cooler (1-1301) by valve V-73. The combined cooled gas stream was at an average temperature of 650°F before entering the first stage shift reactor (1-2502), higher than the target value. The shift feed gas temperature was controlled by manipulating bypass valve V-73.

The adiabatic exothermic shift reaction would increase catalyst bed temperature from 650°F to approximately 800°F. However, the relatively small amount of gas going through the shift catalyst beds did not increase the catalyst bed temperatures during the operation period. The first shift reactor effluent entered the second shift reactor (1-2503) through bypass valve V-34. The second shift reactor effluent, at an average temperature of 580°F entered the desulfurizer for sulfur (H$_2$S) removal. Individual electrical heaters were used in the shift reactors and the desulfurizer to compensate for the heat losses to the surrounding environment. The desulfurized gas was subsequently cooled in the effluent coolers (1-1303A and 1-1303B). The cooled gas/condensate mixture then entered the effluent separator (1-1201) for condensate removal before venting to atmosphere.

During normal operation, surveillance was continuous and data was recorded at 30-min intervals.
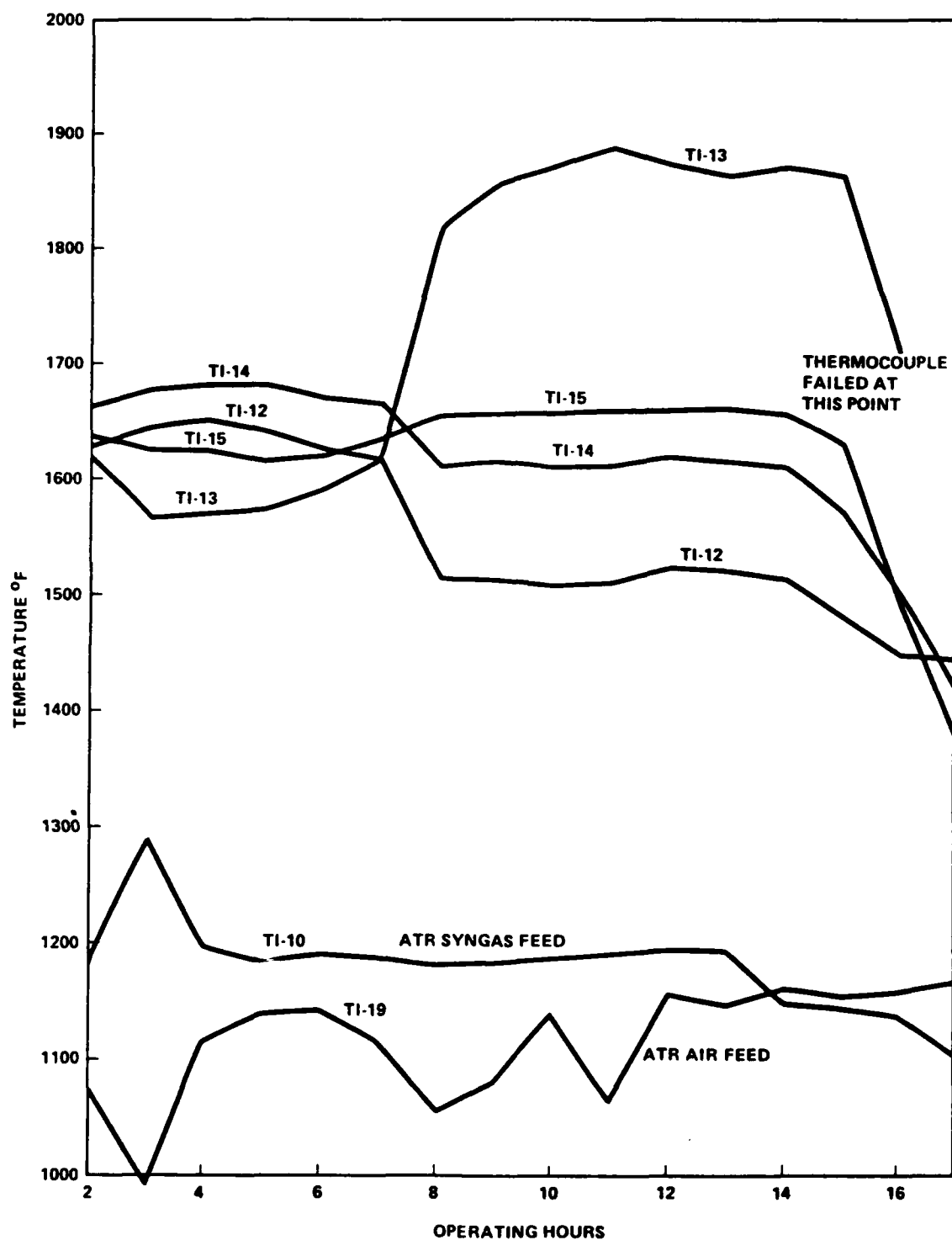
Figure 10. ATR operating temperature profile versus time

D. ANALYTICAL PROCEDURES

Analytical equipment and procedures used have been described in Section 7.
Detailed DF-2 feedstock and feed water analyses are included as Appendix C.

E. HYDROGEN PRODUCTION RUN

All catalysts were in the oxidized state following a DP maintenance
turnaround. Operations were begun by activating the electrical heaters for the
HTSR, ATR, air preheater, shift reactors, knockout drum (1-1204), and the
desulfurizer. Air flow was started through the air preheater; it served as the
heating medium for the catalyst beds during the plant heatup period.

Electric current loadings to the electrical heaters were adjusted to achieve
the following maximum HTSR and ATR catalyst hourly heatup rates.

| Catalyst Temperature | Catalyst Heatup Rate |
|---|---|
| 60°F - 400°F | 50°F |
| 400°F - 1000°F | 70°F |
| 1000°F - 1800°F | 100°F |

Some delays occurred because of electrical heater malfunctions and the HTSR
and ATR catalyst temperatures reached 1000°F after 29 hr. Heat to the steam
superheater (SSH), 1-1405, was then turned on and nitrogen flow started
through it as the first step to bring the SSH on stream. Nitrogen flow
continued until the SSH effluent temperature reached 1000°F at which point the
nitrogen flow was sharply reduced and steam flow started.

The reactors and related DP equipment were brought to operating temperature
and the catalysts conditioned by injecting DF-2 and superheated steam as
described earlier to reduce/presulfide the catalysts. Multiple electrical
heater/controller problems were encountered and resolved during the catalyst
conditioning period.

The DP was placed on stream using the following feed rates for the first 12 hr of full operation:

| Feed Stream | Feed Rate, mole/hr | Reactant-to-Carbon Ratio |
|---|---|---|
| DF-2 | 0.033 (0.50 mole/hr carbon) | - |
| Steam | 3.25 to 3.55 | 6.5 to 7.1 moles steam/atom carbon |
| Air | 0.13 to 0.17 | 0.26 to 0.34 $\frac{\text{moles oxygen}^*}{\text{atom carbon}}$ |

*104% to 136% of design rate.

At the end of the twelfth operations hour, readjustment of the key process parameters was begun with the objective of bringing all parameters to design condition. At the end of the fourteenth operating hour, the key feed rates were:

| Feed Stream | Feed Rate, mole/hr | Reactant-to-Carbon Ratio |
|---|---|---|
| DF-2 | 0.039 (0.58 mole/hr carbon) | - |
| Steam | 2.54 | 4.38 moles steam/mole carbon |
| Air | 0.16 | 0.28 moles oxygen/mole carbon |

The product gas analyses indicated that the DP was producing a product containing 32% to 36.5% hydrogen (see Table 11).

The steam preheater electrical heating system failed after 15-1/2 hr operation, starting a forced shutdown. Heat addition was continued by the other heaters and operation continued through 17 hr operation at which time the ATR heaters failed and the DP was shut down.

TABLE 11.  Operating Data Summary:  Product Gas Analysis.

| Gas Composition | Volumetric Percentage, dry basis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Operating Hours | | | | | | | |
| | 2 | 5 | 7 | 10.5 | 13.5 | 15 | 16 | 17 |
| Hydrogen | 31.90 | 34.30 | 36.60 | 34.80 | 35.30 | 35.10 | 34.84 | 33.85 |
| Carbon Monoxide | 3.30 | 3.44 | 3.51 | 3.41 | 4.58 | 5.61 | 4.63 | 4.20 |
| Carbon Dioxide | 18.60 | 19.10 | 20.10 | 18.30 | 19.90 | 16.50 | 18.43 | 19.87 |
| Methane | 9.06 | 10.20 | 11.50 | 10.60 | 11.40 | 10.90 | 11.39 | 10.65 |
| Nitrogen | 49.08 | 45.10 | 39.37 | 37.10 | 32.60 | 33.27 | 34.71 | 40.53 |
| Total | 111.94 | 112.14 | 110.92 | 104.21 | 103.78 | 101.38 | 104.00 | 109.10 |
| Hydrogen Sulfide | - | - | - | - | - | - | - | 0.34 ppmv |
| Sulfur Dioxide | - | - | - | - | - | - | - | 35.8 ppmv |
| Methyl Mercaptan | - | - | - | - | - | - | - | 10.6 ppmv |
| Dimethyl Mercaptan | - | - | - | - | - | - | - | 91.8 ppmv |

F.  SHUTDOWN OPERATION

The DP experienced a forced shutdown caused initially by the SSH (1-1306)
electrical heater failure. Shortly thereafter, the upper electrical heaters in
the ATR failed. DF-2 fuel and process air feed were first terminated, process
steam flow was continued for 15 min before complete shutdown. This was done to
avoid any carbon deposition on the catalyst beds. The DP was then
depressurized, purged with nitrogen, and allowed to cool to ambient
temperature with all electrical heaters off.

G.  RESULTS OVERVIEW

Data discussed here was developed during the first month's operating period of
the DP. Considering the scope and complexity of the DP equipment and control
systems, this may be classified as a startup period. Emphasis during this
operating phase was on (1) methods of minimizing heat losses at the elevated
temperatures of 1800°F-plus in the small diameter transfer pipe systems, heat

temperatures of 1800°F-plus in the small diameter transfer pipe systems, heat exchangers, and vessels; (2) procedures for achieving and maintaining the high operating temperatures; (3) establishing the performance reliability of the equipment with emphasis on the high temperature electrical heaters and their controllers; (4) establishing proper sensitivity and response characteristics for the instruments and control systems; and (5) increasing the skill level of the operating crew specific to this DP process configuration, equipment, and control system.

The initial operations period resulted in both positive and negative results. The positive results were:

(1) A fuel gas stream containing a significant concentration of hydrogen was produced for a 15-1/2 hr period from commodity-purchased DF-2 diesel fuel doped to contain 0.5% sulfur by weight.

(2) A preliminary operations data base was generated to guide decisions regarding final DP modifications to achieve design performance.

(3) Operations personnel increase their skill level specific to DP performance characteristics.

(4) The data generated indicated that the process configuration can meet the project objectives following completion of changes/improvements defined later in this report.

Negative results included:

(1) Failure of the high temperature electrical heating elements in the SSH (1-1405) and ATR (1-2501) resulted in forced shutdown requiring corrective action before restarting the DP.

(2) Detailed examination of the dissembled ATR after shutdown indicated design and fabrication deficiencies that need correction.

(3) Operating temperature measurements indicated that additional preheating must be supplied to steam, air, and ATR fuel gas feeds to compensate for heat losses and achieve the projected process efficiencies. Also, additional heat input/insulation must be added to transfer lines and vessels to maintain the high operating temperatures.

(4) Adjustments are required to the high temperature sensing and instrumentation systems to assure their longevity.

Interpretations of the data and information developed here are discussed in the following paragraphs. Recommendations designed to achieve the objective of target yields, efficiency, and capacity are also presented.

H. DATA SUMMARY

Summaries of experimental data recorded during the hydrogen production operating period are presented in Table 11, Table 12, and Table 13 and in Fig. 9, Fig. 10, and Fig. 11. Operating temperature profiles of the unit are shown in Table 12 and Fig. 9 and Fig. 10 while Table 13 presents feedrates and key feed mole ratios. Table 13 and Fig. 11 summarize product gas compositions as a function of time.

Axial thermocouple locations in the HTSR and ATR reactors are shown in Fig. 12 and Fig. 13, respectively. These thermocouple numbers correspond to those cited in Fig. 14 and Fig. 15.

TABLE 12. Operating Temperature Profiles Summary.

| Description | Measuring Points | Temperature, °F | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Operating hours | | | | | | | |
| | | 2 | 5 | 7 | 10.5 | 13.5 | 15 | 16 | 17 |
| Superheated Steam | TI-9 | 1056 | 1055 | 1095 | 1199 | 1134 | 1153 | 1115 | 922 |
| HTSR Feed | TI-2 | 447 | 430 | 439 | 454 | -* | - | - | - |
| Temperature | TI-3 | 1478 | 1482 | 1488 | 1334 | 1159 | 1183 | 1302 | 1506 |
| | TI-5 | 1836 | 1850 | 1853 | 1879 | 1869 | 1872 | 1876 | 1878 |
| | TI-7 | 1711 | 1740 | 1747 | 1784 | -* | - | - | - |
| HTSR Effluent | TI-9 | 1266 | 1263 | 1278 | 1296 | 1266 | 1249 | 1251 | 1234 |
| ATR Feed Gas | TI-10 | 1184 | 1181 | 1187 | 1191 | 1174 | 1144 | 1137 | 1102 |
| HTR Air Feed | TI-19 | 1074 | 1137 | 1116 | 1151 | 1156 | 1154 | 1156 | 1166 |
| ATR Bed | TI-12 | 1628 | 1641 | 1616 | 1510 | 1518 | 1480 | 1446 | 1442 |
| Temperature | TI-13 | 1620 | 1574 | 1614 | 1883 | 1878 | 1869 | 1704 | - |
| | TI-14 | 1662 | 1681 | 1666 | 1614 | 1615 | 1574 | 1502 | 1419 |
| | TI-15 | 1636 | 1619 | 1626 | 1660 | 1665 | 1631 | 1492 | 1368 |
| Heat Exchanger | | | | | | | | | |
| 1-1313:    Inlet | TI-17 | 1499 | 1487 | 1479 | 1458 | 1461 | 1451 | 1359 | 1252 |
| Outlet | TI-18 | 1228 | 1228 | 1223 | 1211 | 1201 | 1185 | 1160 | 1070 |
| First Shift | | | | | | | | | |
| Reactor | | | | | | | | | |
| Inlet | TI-33 | 883 | 687 | 667 | 670 | 652 | 616 | 610 | 645 |
| Outlet | TI-20 | 654 | 755 | 696 | 655 | 641 | 626 | 623 | 622 |
| Second Shift | | | | | | | | | |
| Reactor | | | | | | | | | |
| Inlet | TI-34 | 608 | 683 | 636 | 598 | 583 | 563 | 558 | 558 |
| Outlet | TI-21 | 580 | 586 | 614 | 591 | 574 | 568 | 559 | 552 |
| Product Gas | TI-37 | 119 | 120 | 124 | 126 | 114 | 112 | 115 | 115 |

*Thermocouple failed

TABLE 13. Operating Data Summary:  Feed Stream Flow Rates.

| Description | Measuring Points | Operating hours | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 2 | 5 | 7 | 10.5 | 13.5 | 15 | 16 | 17 |
| DF-2 Feed | FI-1 | | | | | | | | |
|   gal/hr | | 0.9735 | 0.9735 | 1.0065 | 0.9735 | 1.155 | 1.1715 | 1.0725 | 0.975 |
|   mole/hr | | 0.032 | 0.032 | 0.034 | 0.032 | 0.038 | 0.039 | 0.036 | 0.032 |
| Process Steam | FRC-2 | | | | | | | | |
|   lb/hr | | 61.83 | 60.32 | 61.83 | 60.32 | 55.04 | 45.99 | 49.01 | 49.01 |
|   mole/hr | | 3.43 | 3.35 | 3.43 | 3.35 | 3.06 | 2.55 | 2.72 | 2.72 |
| Process Air | FFIC-5 | | | | | | | | |
|   stdft$^3$/hr | | 282.0 | 296.1 | 235 | 286.7 | 305.5 | 277.3 | 272.6 | 291.4 |
|   mole/hr | | 0.74 | 0.78 | 0.62 | 0.76 | 0.81 | 0.73 | 0.72 | 0.77 |
| Steam/ Carbon[a] | - | | | | | | | | |
|   mole/atom | | 7.11 | 6.94 | 6.85 | 6.75 | 5.30 | 4.40 | 5.05 | 6.05 |
| Steam/DF-2 | - | | | | | | | | |
|   lb/gal | | 63.51 | 61.96 | 61.43 | 61.96 | 47.65 | 39.26 | 45.70 | 54.01 |
|   mole/mole | | 107.2 | 104.7 | 100.9 | 104.7 | 80.5 | 65.4 | 75.6 | 85.0 |
| Oxygen Carbon[b] | - | | | | | | | | |
|   mole/atom | | 0.324 | 0.340 | 0.261 | 0.329 | 0.296 | 0.265 | 0.284 | 0.359 |
| Air/DF-2 | - | | | | | | | | |
|   stdft$^3$/gal | | 289.7 | 304.2 | 233.5 | 294.5 | 264.5 | 236.7 | 254.2 | 321.1 |
|   mole/mole | | 23.1 | 24.4 | 18.2 | 23.8 | 21.3 | 18.7 | 18.5 | 24.06 |

[a]Design steam-to-carbon ratio: 3 mole/atom
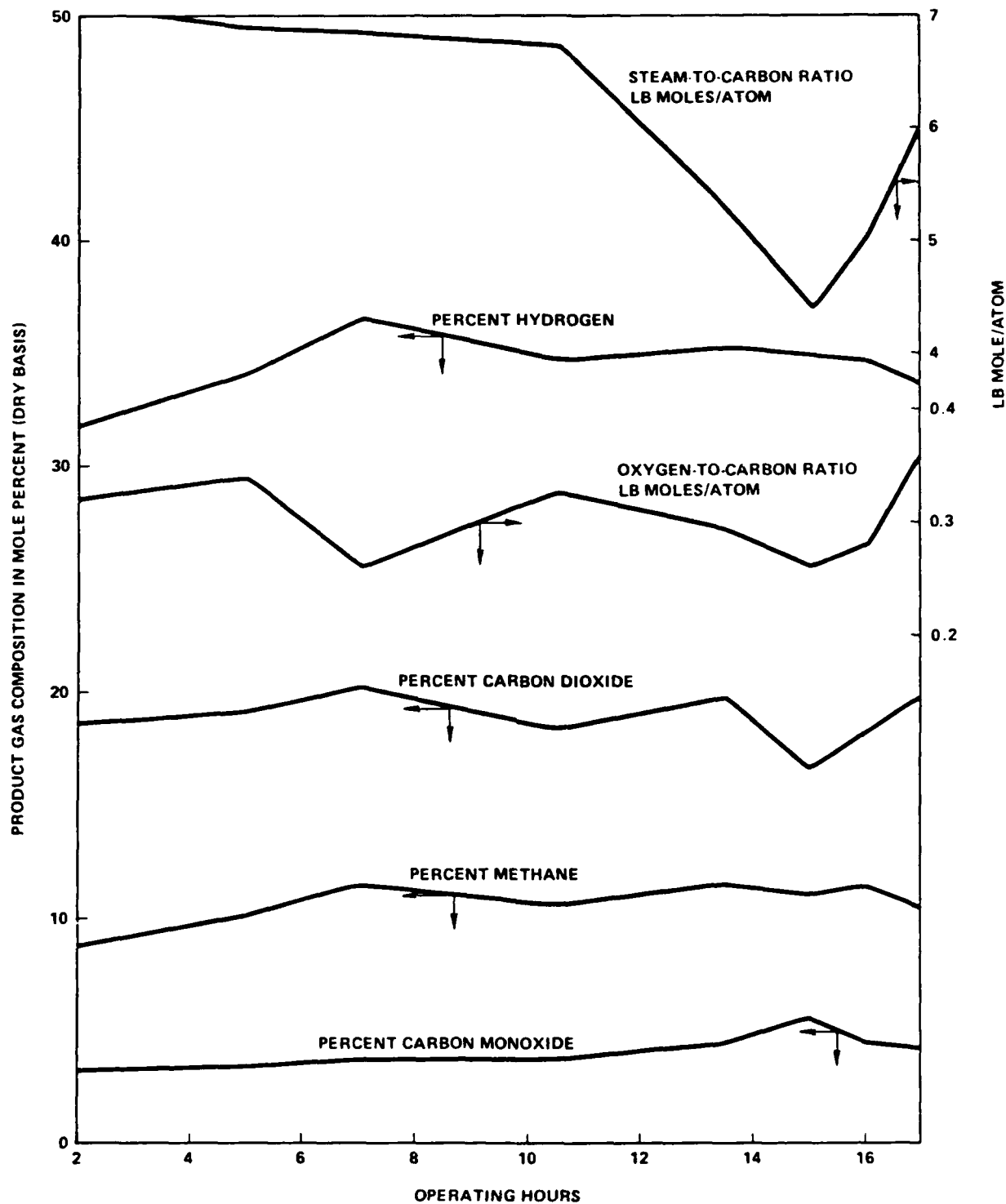[b]Design oxygen-to-carbon ratio: 0.250 mole/atom

Figure 11. Feed rates and gas composition
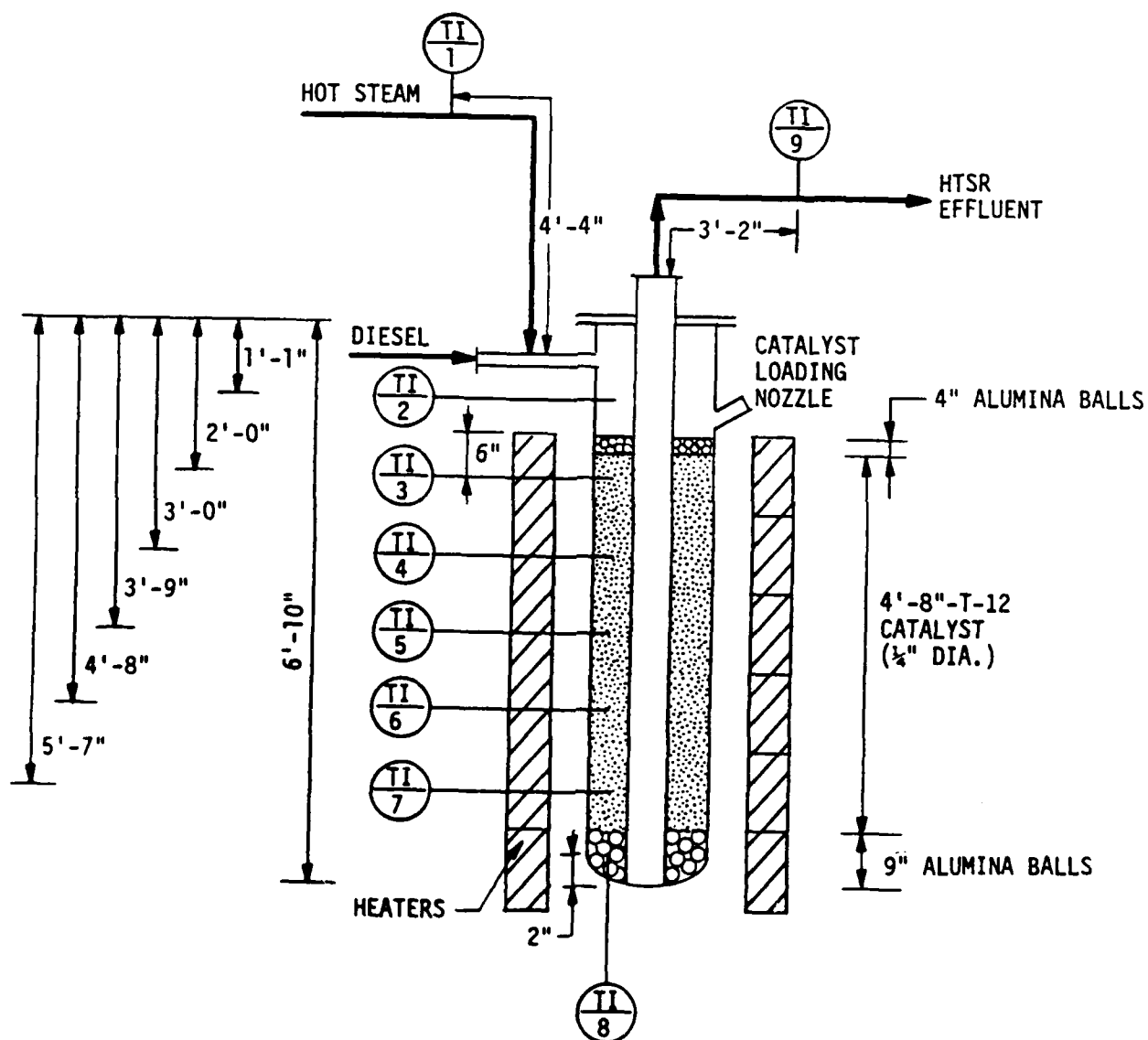as a function of time.

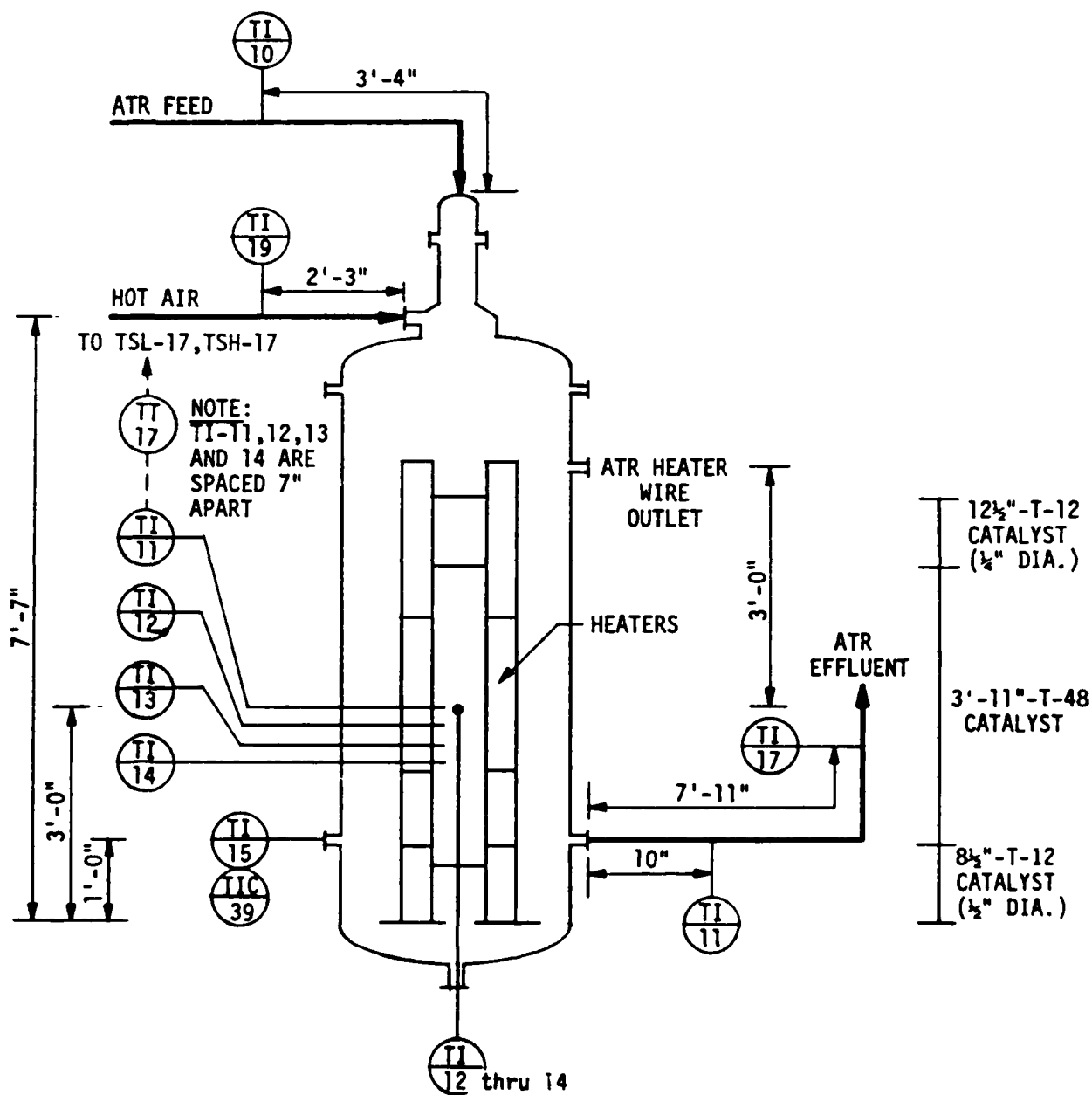Figure 12. **High temperature steam reformer thermocouple and catalyst locations.**

012187

Figure 13. Autothermal reformer thermocouple and catalyst locations.
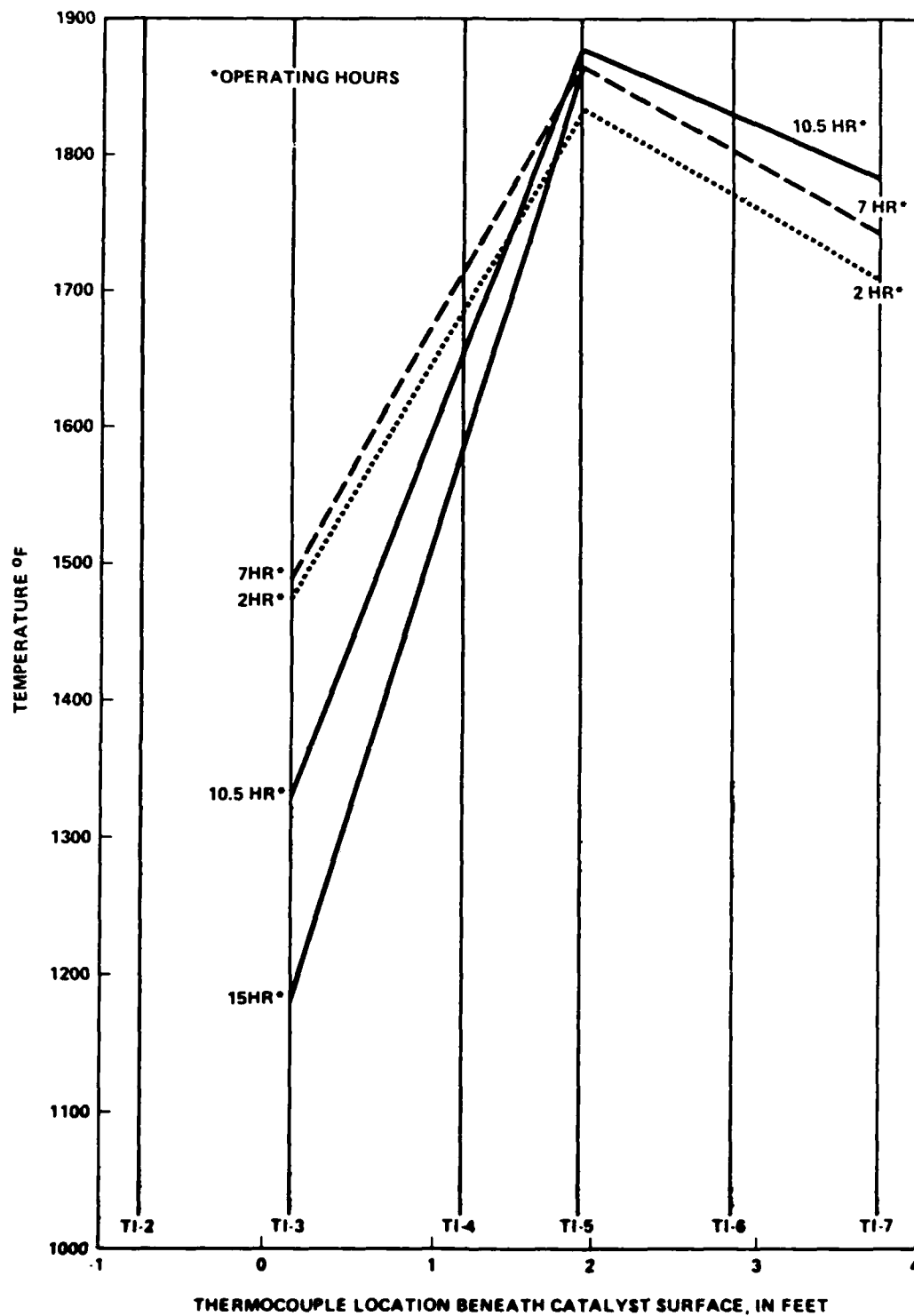
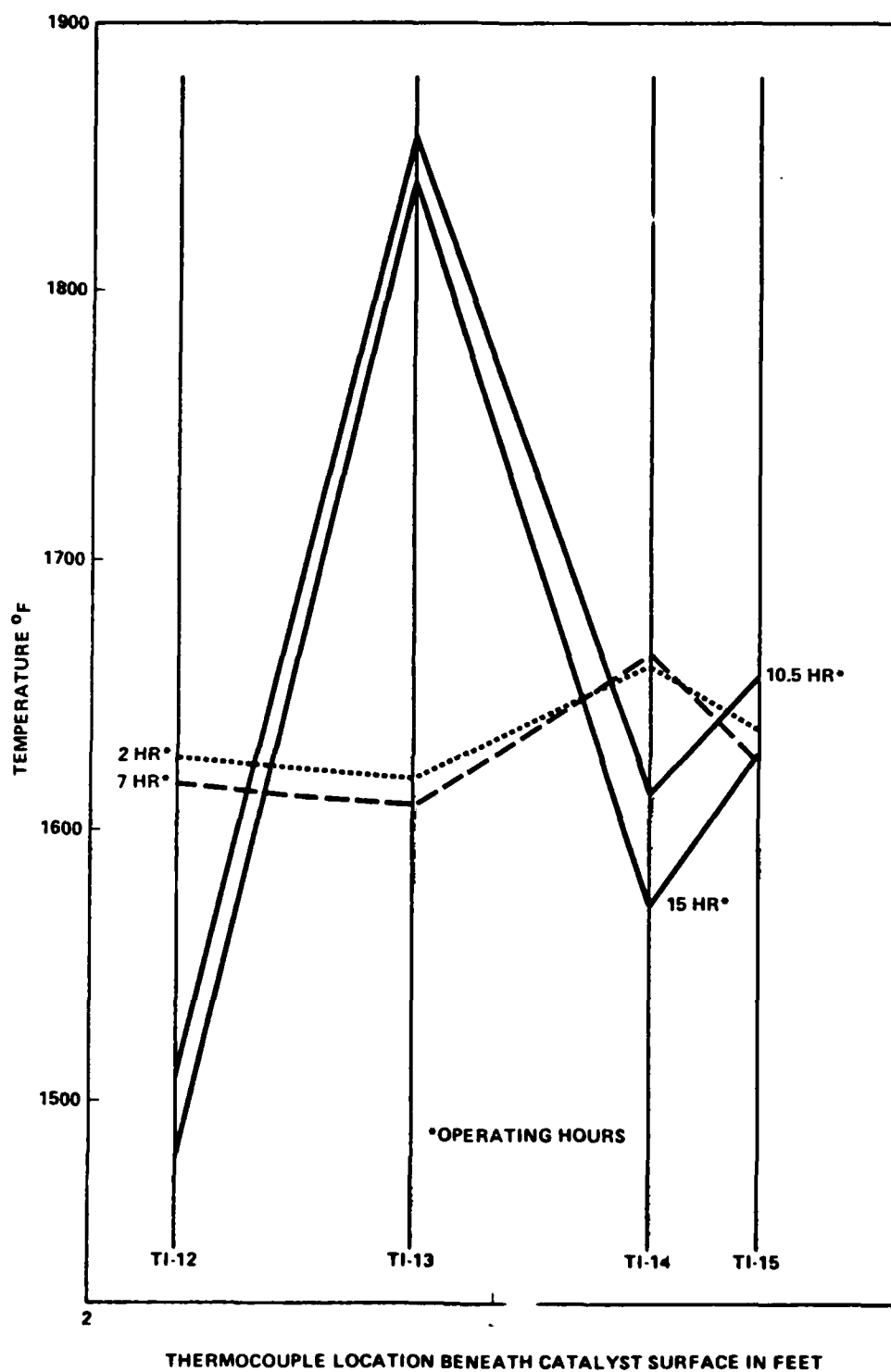Figure 14. **High temperature steam reformer axial temperature profile**.

Figure 15.  Autothermal axial temperature profile.

Calculated product gas flow rates are summarized in Table 14. Separate predictions were based on carbon and nitrogen balances instead of experimental product gas flow rate measurements. The DP was equipped with a gas flow meter (FQI-14) located at the gas exit point (see Fig. 5 in Section 3). Unfortunately, the meter malfunctioned early in the operating period and no product gas flow rates were obtained. Dismantling the gas meter revealed solid deposits that appeared to consist of napthalene and related chemical compounds.

TABLE 14. Calculated Product Gas Flow Rates.

| Description | Operating hours | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 7 | 10.5 | 13.5 | 15 | 16 | 17 |
| Product Gas Flow Rate, stdft$^3$/hr Calculated from Carbon Balance[a] | 661 | 627 | 597 | 590 | 628 | 676 | 608 | 535 |
| Calculated Hydrogen[b] Production, mole/hr | 0.56 | 0.57 | 0.58 | 0.54 | 0.58 | 0.63 | 0.56 | 0.48 |
| Product Gas Flow Rate, stdft$^3$/hr Calculated from Nitrogen Balance[c] | 454 | 522 | 463 | 562 | 672 | 558 | 539 | 514 |
| Calculated Hydrogen[b] Production, mole/hr | 0.38 | 0.47 | 0.45 | 0.52 | 0.63 | 0.52 | 0.49 | 0.46 |

[a]Calculation was based on the assumption that all carbon entering the system exited the system as carbon onoxide, carbon dioxide, and methane in the product gas (Table 11).
[b]Calculated from Table 11, Table 12, and Table 15.
[c]Calculation was based on the assumption that all nitrogen entering the system exited as nitrogen in the product gas.

I. DATA ANALYSIS

Fig. 11 indicates that the hydrogen concentration varied within reasonably narrow limits over the 8-hr time interval from the seventh to fifteenth

operating hour. Gas composition average values, standard deviations, ranges, and range ratio are summarized in the following paragraphs.

The data population consisted of the four product gas compositions listed at operating hours 7, 10.5, 13.5, and 15 in Table 11. At the 95% confidence level, the product gas composition, expressed as mole percent, dry basis, was:

| | | |
|---|---|---|
| Hydrogen | = | 35.45 ± 1.58 |
| Carbon monoxide | = | 4.28 ± 2.06 |
| Carbon dioxide | = | 18.70 ± 3.34 |
| Methane | = | 11.10 ± 0.84 |
| Nitrogen | = | 35.59 ± 6.42 |
| | | |
| Total | = | 105.12 ± 8.18 |

The relative percentage variation was lowest for hydrogen. Additional detail is presented in Table 15.

TABLE 15.  Product Gas Consistency Data.

Reference: Table 11 operating hours 7 to 15.

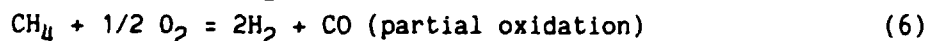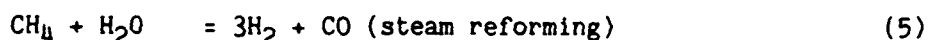| Component | Average Mole % | Standard Deviation | Range | Range Ratio* |
|---|---|---|---|---|
| Hydrogen | 35.45 | 0.79 | 34.80-36.60 | 1.05 |
| Carbon Monoxide | 4.28 | 1.03 | 3.51-5.61 | 1.60 |
| Carbon Dioxide | 18.70 | 1.67 | 16.50-20.10 | 1.22 |
| Methane | 11.10 | 0.42 | 10.40-11.50 | 1.11 |
| Nitrogen | 35.59 | 3.21 | 32.60-39.37 | 1.21 |
| Total | 105.12 | 4.09 | 101.38-110.92 | 1.09 |

*Ratio Maximum/Minimum Reading

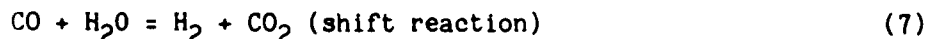The Table 15 measured average gas compositions compare with design values as follows:

| Component | Design | Experimental |
|---|---|---|
| Hydrogen | 55.48 | 35.45 |
| Carbon monoxide | 1.30 | 4.28 |
| Carbon dioxide | 22.03 | 18.70 |
| Methane | 0.10 | 11.10 |
| Nitrogen | 21.09 | 35.59 |
| | 100 | 100 |

Inspection shows that three factors will be required to achieve the hydrogen purity of 50%, minimum, dry basis:

(1)  Reduce the methane content by the reactions:

$$CH_4 + H_2O = 3H_2 + CO \text{ (steam reforming)} \qquad (5)$$
$$CH_4 + 1/2\ O_2 = 2H_2 + CO \text{ (partial oxidation)} \qquad (6)$$

(2)  Reduce the carbon monoxide content by the reaction:

$$CO + H_2O = H_2 + CO_2 \text{ (shift reaction)} \qquad (7)$$

(3)  Reduce the nitrogen content by control of air feed rate to the ATR.

Each of the above improvements are achievable using the teachings of industrial hydrogen plant experience and reported research and development results for the process system being demonstrated. To illustrate the impact of the changes, Table 16 summarizes the postulated compositions based on converting all methane reported in Table 15 to hydrogen and carbon monoxide and 90% of carbon monoxide to hydrogen and carbon dioxide. The hydrogen content in each of the Table 16 adjusted compositions exceeds the required 50 mole percent minimum and the compositions compare favorable with the Table 1

design targets. We, therefore, conclude that when the methane leakage is reduced to its proper level of 0.1 mole percent and the shift reaction is performing satisfactorily, the process configuration will achieve its objectives. This conclusion is consistent with the reported experience of the catalyst suppliers.

TABLE 16.  Postulated Product Gas Compositions.

| Component | Operating Hours | | | |
| | 7 | 10.5 | 13.5 | 15 |
|---|---|---|---|---|
| Hydrogen | 58.18 | 53.22 | 55.05 | 55.50 |
| Carbon Monoxide | 0.94 | 1.00 | 1.05 | 1.11 |
| Carbon Dioxide | 21.13 | 21.13 | 22.50 | 21.06 |
| Methane | 0 | 0 | 0 | 0 |
| Nitrogen | 24.75 | 24.65 | 21.40 | 22.34 |
| Total | 100.00 | 100.00 | 100.00 | 100.00 |

Note: The product gas compositions were postulated using Table 11 data and the assumptions that (1) all methane in the operating data is converted to carbon monoxide and hydrogen and (2) 90% of the resultant carbon monoxide content is water gas-shifted to hydrogen and carbon dioxide.

J.  HYDROGEN PRODUCTION RATE

As mentioned earlier, the product gas flow meter malfunctioned early in the test run and was bypassed for the remainder of the run. However, the feed rates for DF-2 and air were measured and the system was pressure tested before the start of the run to assure no leakage, thereby providing the basis for indirect prediction of flow rates by nitrogen and carbon balances.

The nitrogen input to the DP came from the air feed to the ATR and the DF-2 with the DF-2 nitrogen representing approximately 1% of the total input. The nitrogen content of the product gas was measured by gas chromatogi .,    By writing total material balances and nitrogen balances, the flow rate of the product gas stream was predicted.

Similarly, the carbon input to the DP came from the DF-2 feed and the carbon effluent was in the form of carbon monoxide, carbon dioxide, methane, and higher hydrocarbons. The carbon feed rate was approximately 6 lb/hr or greater than 100 lb for the total run. Observations showed that some carbon-containing solids collected in the effluent line; these would be a small percentage of the feed carbon. Another factor was the possibility of carbon laydown. The ATR was dismantled after the run and some carbon deposition had occurred; however, it was a very small percentage of the more than 100 lb of carbon feed. Still another factor was the possibility of carbon deposition in the system other than the ATR. Pressure drop measurements indicated no significant increase in pressure drop across the system during the course of the run, again indicating that the quantity of carbon buildup should be a small percentage of the total processed by the system.

The use of nitrogen and carbon balances to predict product gas flow rates, as discussed above, provides a mechanism to predict the hydrogen production rate and compare that value with the design rate. While flow rate predictions based on the elemental balances are not 100% accurate, they do provide guidance in the absence of direct product flow rate measurement.

Estimated moisture-free gas flow rates based on carbon and nitrogen balances were presented in Table 14. The averages for the 8-hr operating period from the seventh to fifteenth hour were:

| Estimating Method | Average Flow Rate, stdft$^3$/hr | Standard Deviation | Range | Range Ratio |
|---|---|---|---|---|
| Carbon Balance | 623 | 39 | 597-676 | 1.13 |
| Nitrogen Balance | 564 | 85 | 463-672 | 1.45 |

The ratio of average flow rates (carbon balance/nitrogen balance) was 1.10. At the 95% confidence limits, the average flow rate was:

Carbon Balance   = 623 ±78

Nitrogen Balance = 564 ±170

Pairing the above carbon-balance based average moisture-free product gas rate with the average moisture-free hydrogen concentration shown in Table 15 results in an estimated average hydrogen production rate of 0.58 lb mole/hr. Using the nitrogen-balance average gas rate indicates 0.53 mole/hr hydrogen. This represents approximately 30% of the hydrogen design production capacity at the operating pressure.

Operations at this rate was a startup decision. The unit is capable of significantly higher capacity operation.

K. SPACE VELOCITY

Based on the measured average feed rates, the product gas compositions, the estimated product gas rate, and the geometry of the DP catalytic beds, the experimental space velocities compare with design as follows:

| Reactor Designation | Estimated Experimental Space Velocity, $hr^{-1}$* | Design Space Velocity per Actual DP Catalyst Loading, $hr^{-1}$ |
|---|---|---|
| HTSR | 2430 | 2180 |
| ATR | 3340 | 3540 |
| First Stage Shift Reactor | 460 | 490 |
| Second Stage Shift Reactor | 660 | 690 |
| Desulfurizer | 200 | 210 |

*See Table 4.

These results confirm that the DP is capable of operating at its design capacity.

## L.  REACTION CONDITIONS

The DP was operated at a feed pressure of 60 psig and a product delivery
pressure of 20 psig.

Temperatures in both the primary reformer (HTSR) and secondary reformer (ATR)
exceeded the 1800°F target within the reactor bed; see Fig. 9 and Fig. 10.
However, Fig. 14 and Fig. 15 show that the measured temperature peaked at a
midpoint in the catalyst bed. In both instances, the indicated temperature at
the entry to the catalyst bed was below the target of 1800°F, minimum. For
effective conversion, the reactants should be at the 1800°F level throughout
the catalyst bed.

## M.  OPERATIONS DISCUSSION

Investigation indicated the potential for partial thermal cracking in the
vapor space above the catalytic bed in the HTSR. If confirmed, this could have
been a contributor to the low hydrogen concentration. Also, olefins, which are
a product of cracking reactions as well as a potential product from T-12
catalysis, are a precursor to mercaptan formation.

Fig. 9 indicates that the T-12 catalyst may not have been fully conditioned
before the start of operations.  HTSR TI-3 remained relatively constant at
1475°F-1500°F for 7 hr, then dropped approximately 200°F over the next hour.
This indicates a significant increase in the endothermic steam reforming
reaction may have occurred at that time. In a related observation, the high
product carbon monoxide content indicates that the shift catalyst may also not
have been fully conditioned before the start of operations.

Fig. 10 indicates that the ATR's TI-12, similarly to TI-3 in the HTSR, saw a
significant drop in temperature between the seventh and eighth operating
hours. This may well have been caused by an increased endotherm because of
increased reforming in the T-48 catalyst bed. The increased endotherm may have
been caused by the catalyst being further conditioned at that time, having
been incompletely conditioned before startup.

SECTION 9

EQUIPMENT PERFORMANCE

A. ELECTRICAL HEATERS

The high temperature electrical heating systems, including the heating
elements and the controllers, caused the highest incidence of operating
problems. The initial and direct cause of the forced shutdown for the hydrogen
production run was the failure of the electrical heaters for the steam
superheater (SSH), 1-1306. Before the failure, neither the SSH nor the air
preheater (1-1404) proved themselves capable of reaching their design exit
temperature of 1300°F and 1400°F, respectively. Each of the controllers
exhibited instability during the brief operating periods; we anticipate that
these controller problems can be eliminated.

B. AUTOTHERMAL REFORMER

The autothermal reformer (ATR) electrical heaters failed at the end of the
test run, approximately 1-1/2 hr after the SSH failure. The reactor was
disassembled for inspection, analysis, and repair and the following
observations recorded:

(1) The physical appearance of the refractory combustion channel located
at the exit of the burner indicated preferential combustion on half
of the circular area and very little combustion on the other half.

(2) The inner surface of the clamshell, or doughnut, electrical heaters
indicated combustion in the annular space formed by the outer
periphery of the catalyst tube and the inner surface of the
electrical heaters.

(3) The upper electrical heater, and high nickel heating wires, were
burned in such a way to indicate that they had been exposed to
temperatures in excess of 2200°F.

(4) Product gas analysis showed high methane content and some three times
as much sulfur dioxide as hydrogen sulfide.

Analysis of these observations and data led to the following hypotheses
regarding ATR performance:

(1) Hot air feed was not uniformly distributed to the burner, resulting
in combustion in the 180° arc closest to the air feed pipe entering
the burner.

(2) Combustion at the burner tip was not complete. The below-design
temperatures of the air and fuel gas feeds to the burner contributed
to this phenomena. To illustrate, the design and actual air feed
temperatures to the ATR were 1400°F and 1100°F-1200°F, respectively.
Similarly, design and actual feed temperatures for the fuel gas
were 1650°F and 1200°F, respectively. The nonuniform air
in the burner, discussed under Item 1, is also thought to be a
contributing factor to the subpar combustion performance.

(3) A portion of the reactant gases bypassed the
through the annular space formed by the
catalyst tube and the inner surface
flow pattern, combined with delayed
methane and sulfur dioxide content, as
analyses shown in Table
high methane leakage.

Procedures for eliminating each
developed. Additional details are

C. OTHER PROBLEM AREAS

Heat losses from high temperature
can be reduced to the
plus electrical heat

PCD/6629
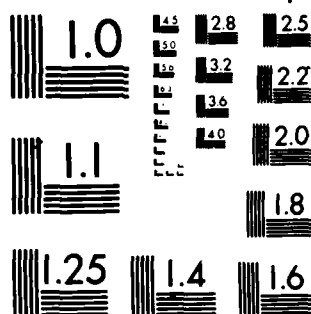
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

The product gas stream must be free of solids before entering the gas flow meter FQI-14. Gas cleaning can be done by quenching, scrubbing, and filtering the gas feed to FQI-14. This will eliminate napthalene and related compounds from the gas stream.

The air preheater equipment supplier has recommended that the junction boxes serving the electrical heaters be air cooled to improve performance and eliminate the erratic behavior of the heater/controller system. This cooling system has been installed.

The mechanical performance of the remainder of the DP equipment appeared to be satisfactory. Completion of the limited number of revisions defined in this report is expected to result in reliable continuous operation.

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SECTION 10

CONCLUSIONS

Based on the results of the work reported here, we conclude:

(1)  A process design has been developed that has the potential to achieve
     project goals. This process configuration uses sour reforming to
     process the high sulfur logistic fuels feedstock followed by shift
     reaction and desulfurization.

(2)  Additional operations are required to adequately demonstrate the
     performance of the process configuration. the one month's operating
     time was not adequate because of startup problems, primarily with
     high temperature electrical heaters.

(3)  A 17 hr operating run was completed. The results indicate that the
     demonstration plant (DP) can produce a hydrogen-containing product
     gas with less than 1 p/m (volume) hydrogen sulfide.

(4)  Product hydrogen concentration was of the order of 35 mole percent.
     Contaminants exhibiting higher-than-design concentrations included
     methane, carbon monoxide, and nitrogen. Control of these constituents
     as described below will produce a product gas with at least 53%
     hydrogen, which will meet the project objectives:

     (a)  Convert all methane to oxides of carbon plus hydrogen in the
          high temperature steam reformer (HTSR) and autothermal reformer
          (ATR).

     (b)  Convert 90% of the carbon monoxide co hydrogen by reaction with
          steam in the shift reactors.

     (c)  Reduce the air feed rate to the ATR.

Each of the above changes are achievable.

(5) Failures of high temperature electrical heaters caused forced shutdown of the DP. Design deficiencies of the ATR contributed to failure of the ATR electrical heaters.

(6) Equipment modifications/additions/repairs have been defined, which are judged adequate to provide confidence that the DP can operate reliably to demonstrate the performance of the process configuration.

(7) Candidate materials of construction have been defined for the 1800°F-plus operation in sulfur-containing environments. These materials performed satisfactorily for the brief operating period.

(8) Solids, tentatively identified as napthalene and related compounds, collected in the product gas exist area, causing a malfunction of the product gas meter. To eliminate/control these compounds, oxidation conditions must be controlled in the process and procedures incorporated to assure delivery of clean product gas to the fuel cell.

SECTION 11

RECOMMENDATIONS

Recommendations for future operation and modifications to equipment and procedures are summarized below. These recommendations incorporate the results of (1) the operations experience summarized in the preceding report sections, (2) commercial hydrogen plant design/operations experience, and (3) inputs from the experience reported by other workers, domestic and international, for conversion of dis⁺illate hydrocarbon liquids to hydrogen-rich fuel gas.

A.  OPERATION

Modify and improve the demonstration plant (DP) as described below, then resume operations to demonstrate that the process configuration tested is capable of efficiently and reliably producing a specification hydrogen-rich gas stream from logistic fuels suitable for use in a phosphoric acid fuel cell (PAFC).

B.  AUTOTHERMAL REFORMER (ATR)

(1)  Install distribution fins in the hot air burner feed annular space. Weld fins to the outer surface of the central burner tube that transports the hot fuel gas to the burner tip. The increased pressure drop generated by the fins will result in a uniform flow profile for the air feed to the burner tip, ensuring uniform combustion.

(2)  Insert a refractory tube to form a confining boundary for the combustion zone. Insert the tube to surround the burner tip and to form a positive boundary from the burner tip to the catalyst surface. This is shown in detail in Fig. 16 and Fig. 17. The material of construction should be high purity alumina.

In addition to forming a combustion zone boundary, the tube will serve to minimize reactant bypassing of the ATR catalyst bed.

(3) Insert a seal ring at the top of the ATR to eliminate reactant catalyst bed bypass. The bottom edge of the seal ring is to be welded to the top plate of the catalyst tube and the top edge to seat between the vessel shell inner refractory lining and the metal shell of the vessel head shroud (see Fig. 16). Material should be RA 330 or equivalent. This seal ring should prevent combustion gas/reactant from bypassing the catalyst bed and damaging the electrical heaters.

(4) Increase the fuel gas and air feed temperatures to their design values of 1650°F and 1400°F, respectively. Do this by a combination of heat addition to the transfer lines and improved insulation.

(5) Eliminate the top 12 in. heater section and replace it with Kaowool insulation. This minimizes potential for heater burnout near the combustion zone.

(6) Switch the ATR heater temperature control from TIC-39 to TI-11. This allows more positive control of the heaters in response to the process heat demand.

(7) Replace the failed electrical heaters.

C. HIGH TEMPERATURE STEAM REFORMER (HTSR)

Install additional heaters to maintain the full length of the catalyst bed at 1800°F, minimum. The addition would increase the heat input at the top section, which would increase the DF-2 conversion and decrease the hydrocarbon leakage through the catalyst bed.

D. STEAM SUPERHEATER (SSH)

Replace SSH 1-1405. Two primary alternatives exist:

(1) Fired heater.
(2) A packaged, performance-warranted electrically heated unit.

MACHINE FLANGE FROM 3" THICK PLATE MATL RA-330 FOR FLANGE BOLTS (NUTS, NT-310 S.S. OVAL RING GASKET.

6" × 4" REDUCING TEE STD WT (.28" WALL)

16" STD WT PIPE CAP (.375" WALL) TYP TOP & BOTTOM

2" THICK CERAMIC WOOL

16" 150# R.F. WELD NECK BODY FLANGES

1" FIREBRICK

HEATER CONN RIGID STEEL ELEC CONDUIT (1" ELEC THRD) BY OTHERS

4" O.D. 1 1/8A × 1 1/2" LONG HIGH ALUMINA TUBE INSERT (21 GUAGE)

16" STD WT PIPE (.375" WALL)

HEATER

CERAMIC BALLS

1" PIPE (.109" WALL) MATL RA 330 (SEE NOTE 2)

RETAING RINGS (.109" THK (TYP)

6" 150# R.F. WELD NECK FLANGES

12 1/2" O.D. SHROUD

4" O.D. INSERT

4 3/8" O.D. TUBE RA 330
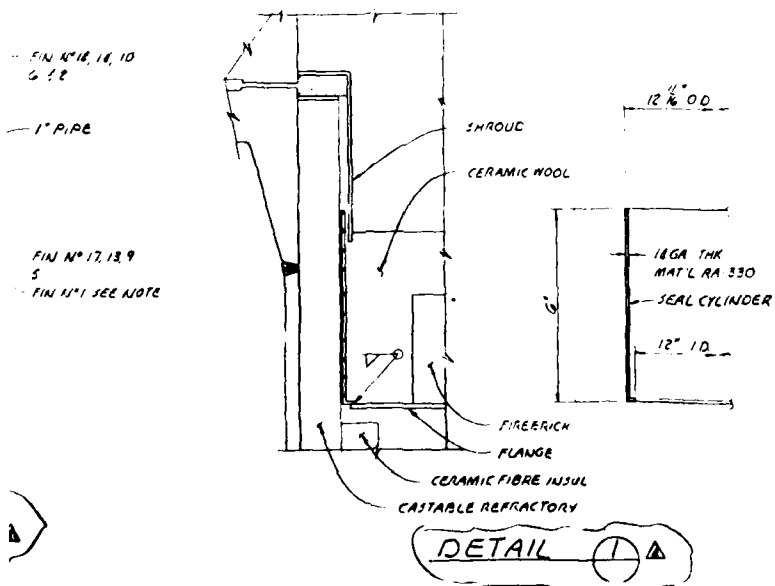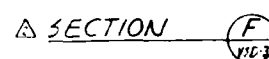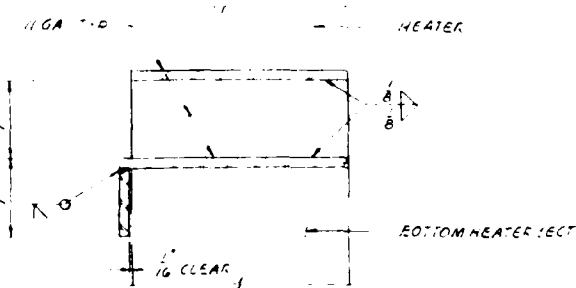
13" I.D. CASTABLE REFRACTORY

CASTABLE REFRACTORY

1'-7" TAN LINE

CERAMIC WOOL

SEAL

1" STD WT PIPE (.109" WALL) RA-330 THERMO WELL NT-304 SS F LINE FLANGE

5" R. SUPT LUG (2) REQD

8" GASKET ALLOW

9 1/8"

8 N.E. 17 SPACES AT 1" = 1'-5"

8" GASKET ALLOW

8"

1'-4"

2'-0" HEATER SECTIONS (2 REQ D

1'-0" FLG FACE / FLG FACE

1'-6"

2'-2" FLG FACE / FLG FACE

9"

1'-9"

2'-0" CERAMIC BALLS

2'-0" CATALYST BED

6'-11" FLG FACE / T

11'-1" OVERALL

CL SUPPORT BEAM

N₁ TOP

PIPE SHELL

BODY FLANGES

N₂ BOTTOM

1'-5" (TYP)

1'-9 3/8" (TYP)

1'-2"

CL SUPPORT BEAM

2" 4"

6"

N₃ N₄

CL 5/8" Φ HOLES IN SUPT LUG FOR 3/4" Φ BOLTS (TYP)

**PLAN A**

2 3/5" OD FINS

FIN N° 18, 16, 10 6 & 8

FIN N° 15, 11, 7 & 9

1" PIPE

FIN N° 16, 12 6 & 8

FIN N° 17, 13, 9 5

FIN N° 1 SEE NOTE

90° FIN SEGMENTS

CL NOZZLE N2

FINS ARE 11GA × 1/2" WIDE MATERIAL RA 330

NOTE FIN N° 1 ONLY 1/16" WIDE

**SECT B**

Figure 16.  Autothermal reformer reactor,
design modification details.

DETAIL ①  REF
V50-2

DETAIL ②  REF
V50-2

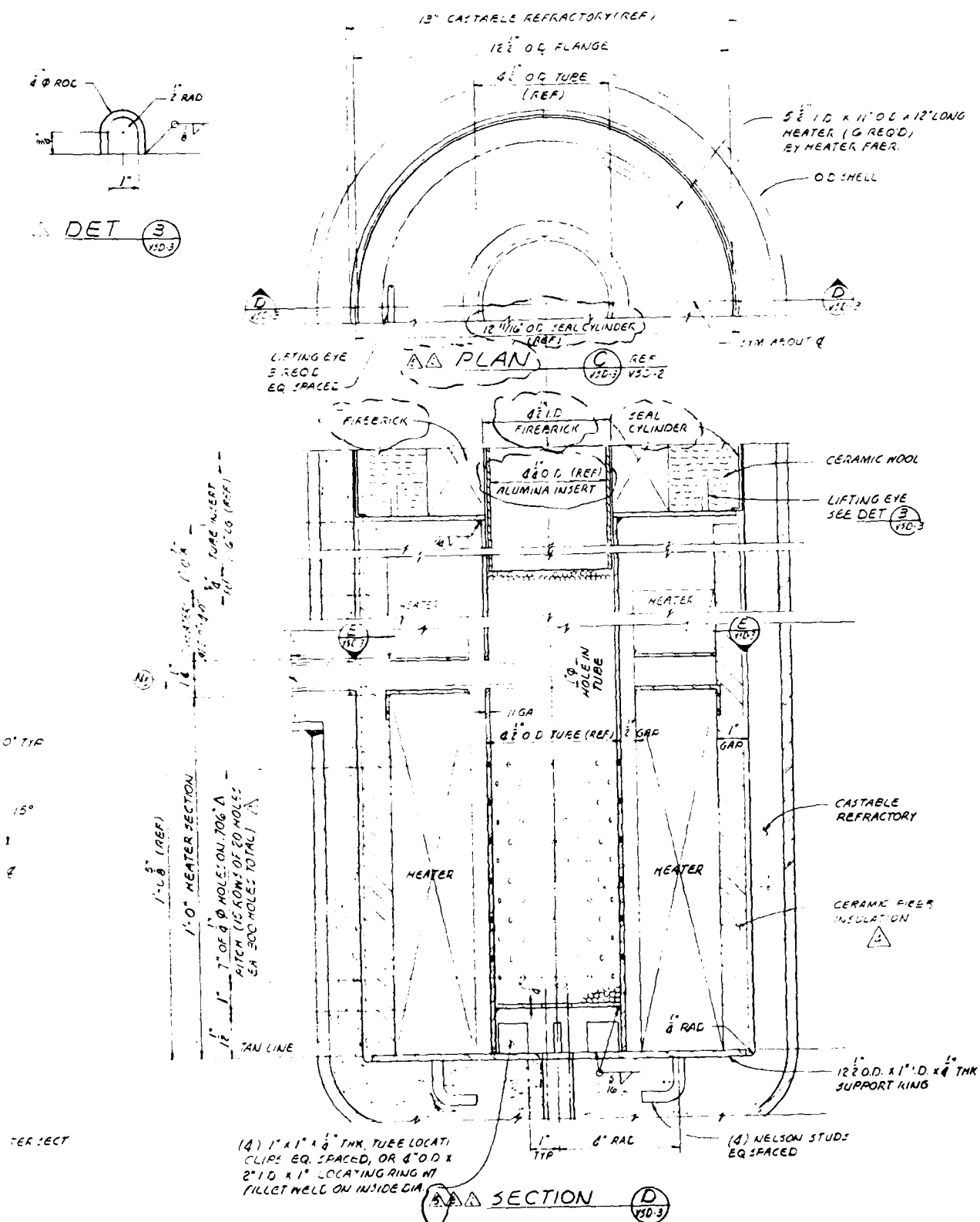PLAN Ⓐ

SECTION Ⓑ
FIREBRICK

PLAN Ⓔ

SECTION Ⓕ

Figure 17. Autothermal reformer reactor, design modification sections and details.

E. REFORMER FEED TEMPERATURES

Install a combination of heaters and supplemental insulation to assure that
the following design feed temperatures are achieved:

(1) 1300°F superheated steam temperature feed to the HTSR.
(2) 1400°F air feed temperature to the ATR.
(3) 1650°F fuel gas (HTSR effluent) feed temperature to the ATR.

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APPENDIX A

SAFETY AND PRELIMINARY HAZARDS ANALYSES

1. SAFETY

A preliminary system safety program was developed early in the project to
define the objectives and procedures for a hazard analysis to assure safe
design and operation of the demonstration plant (DP).  This plan was
implemented by a preliminary hazards analysis (PHA), which contributed to
definition of safety equipment to be installed and procedures to be followed
to assure safe operation of the DP.  Key safety equipment provided for the DP
is listed in Table A-1.

TABLE 1.  List, Key Demonstration Plant Safety Equipment

| Item Number | Description |
| --- | --- |
| 1 | Carbon Monoxide Concentration Monitor |
| 2 | Hydrogen Concentration Monitor |
| 3 | Automatic Sprinklers |
| 4 | Fire Extinguishers |
| 5 | First Aid Kit |
| 6 | Safety Blankets |
| 7 | Safety Shower |
| 8 | Eye Wash Fountain |
| 9 | Hard Hats |
| 10 | Gloves |
| 11 | Safety Glasses |
| 12 | Emergency Lighting |
| 13 | Area Forced Ventilation |
| 14 | Electrical Equipment Grounding |
| 15 | Explosion Proof Electrical Rating |
| 16 | Safety Ladder |

2. PRELIMINARY HAZARDS ANALYSIS

A. Introduction.

The PHA performed on the DP having a capacity of 2 mole/hr of hydrogen is documented in the attached worksheets presented as Table A-2. In these worksheets, an assessment of risk is made for each identified potential hazard. The assessment is performed with and without the implementation of specific corrective/preventive safety measures to demonstrate the effectiveness of the safety measures in reducing risk. The status column will document the implementation of the safety criteria, upon Government review and approval.

B. Methodology.

The PHA was performed in accordance with MIL-STD-882B, Task 202 (see Table A-2). Hazards associated with the proposed DP design or procedures were evaluated for hazard severity and hazard probability. The basis for the analysis was DP design documents, drawings, and model. The piping and instrumentation drawings (P&IDs) provide the level of component detail to be included in the PHA.

TABLE A-2. Preliminary Hazard Analysis Worksheet for Demonstration Plant
System Safety Program

| Subsystem | Failure Mode/Hazard Description | Effect | Risk Level Sev | Prob | Corrective/ Preventive Measures | New Risk Level Sev | Prob |
|---|---|---|---|---|---|---|---|
| Feed Tank | Manual filling operator over-fill tank, flammable liquid hydro-carbon spill | Fire/ explosion | II | B | Level gage operator training | II | C |
| Water feed steam generator | Overpressure | Explosion | II | B | Pressure relief valve on generator | II | B |
| Fuel feed pump | Flammable liquid hydrocarbon leak | Fire/ explosion | II | B | Operator training | II | C |
| | Fails to operate | No fuel to HTSR damage to HTSR catalyst | III | B | Flow indicator interlocked will heat to HTSR | III | C |
| HTSR | Overpressure DP-190 psig Rupture - HTSR - Explosive and Hazardous gases and materials. Very hot 1800°F leaks | Damage to facilities Hazard to personnel | I | B | PSV-6 | I | C |
| | Formation of Nicarbonyl | | I | B | Flush with inert gas on shutdown | I | C |
| Air compressor | | | III | C | | III | C |
| Air heater | | | II | C | | II | C |
| HTSR/ATR EFF HT Exchanger 190 psig | Leak flammable hazardous gases | Fire/ explosion | I | C | Temperature indicators, operator train-ing hydrogen detectors in experiment area PSV 1 | II | C |

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TABLE A-2. Preliminary Hazard Analysis Worksheet for Demonstration Plant
System Safety Program (Contd)

| Subsystem | Failure Mode/Hazard Description | Effect | Risk Level Sev | Risk Level Prob | Corrective/ Preventive Measures | New Risk Level Sev | New Risk Level Prob |
|---|---|---|---|---|---|---|---|
| ATR DP 190 psig DT 1820°F | Leak flammable hazardous gases | Fire/ explosion | I | C | Temperature and pressure indicator | | |
| Waste heat boiler | Leak water into gases | | | | Keep gas pressures higher than coolant pressure | | |
| Knockout drum | Temperature 550°F DP 90 psig DT 575°F Manual drain valve left open - hot hazardous gases escape | Fire/ harm to personnel | I | C | Operator, training | I | C |
| First shift reformer | DP 85 psig DT 735°F gas leak | Fire/ harm to personnel | II | C | Temperature and pressure indicators PSV 2 | II | C |
| Second stage shift reformer | DP 85 psig DT 600°F gas leak | Fire/ harm to personnel | II | C | PSV 3 | II | C |
| Desulfurizer zinc oxide filled | DP 85 psig DT 600°F Formation of this by reaction of hydrogen and zinc sulfide | | II | B | Flush with inert gas manual hazardous gas detector | II | C |

The following hazard categories and probability levels defined in MIL-STD-881B, Appendix A were used in qualitatively assessing the risk of each identified potential hazard:

| Severity Category | Definition |
|---|---|
| I | Catastrophic - may cause death or system loss. |
| II | Critical - may cause severe injury, severe occupational illness, or major system damage. |
| III | Marginal - may cause minor injury, minor occupational illness, or minor system damage. |
| IV | Negligible - will not result in injury, occupational illness, or system damage. |

| Probability Level | Definition |
|---|---|
| A | Frequent - likely to occur frequently. |
| B | Reasonably Probable - will occur several times in the life of an item. |
| C | Occasional - likely to occur sometime in life on an item. |
| D | Remote - so unlikely, it can be assumed that this hazard will not occur. |

In performing the PHA, the hazard severity and accident probability of a particular upset condition was first assessed without regard to any corrective/preventive measures that may be available. Then, assuming these particular safety measures are incorporated into the DP design, the PHA reassesses the hazard severity and accident probability. Safety measures that

are found to be effective in reducing system risk will be identified as safety design and operating criteria.

C. Summary.

Hazards associated with the DP are:

(1) Hazardous Materials:

(a) Hydrogen ($H_2$) is a colorless, odorless, flammable gas. It is nontoxic but can act as an asphyxiant by displacing air. It has a 4% to 75% flammable range. Hydrogen is noncorrosive, but vessels and piping should be designed with safety factors conforming with the ASME code for pressure piping. At elevated temperatures and pressures, possible hydrogen embrittlement adds difficulties to normal equipment design.

(b) Carbon monoxide (CO) is a colorless, odorless, flammable toxic gas with no warning properties. It has a flammable range of 12.5% to 75%. The best prevention of carbon monoxide poisoning is good ventilation.

(c) Hydrogen sulfide ($H_2S$) is a colorless, highly toxic, flammable gas. In low concentration it has a highly distinctive rotten egg odor. It has a 4% to 46% flammable range.

(d) Carbon dioxide ($CO_2$) is a colorless, odorless, low toxicity gas. In low concentrations it acts as an asphyxiant by displacing air. In high concentration it can paralyze the respiratory system.

(e) Nitrogen ($N_2$) is nontoxic, but can act as an asphyxiant by displacing air.

(f) When carbon monoxide (CO) at 210°F to 400°F comes in contact with metallic catalysts, carbonyls can be formed. These carbonyls, especially nickel carbonyl [$Ni(CO)_4$], are severe health hazards. Operating parameters and procedures for startup and shutdown of the process must include either flushing the carbon monoxide from the process equipment with an inert gas or by maintaining the temperature of the reaction vessels above the carbonyl formation zone.

(g) Liquid hydrocarbon fuel such as DF-2 is a flammable liquid. Spills and leaks must be minimized.

(2) Other Hazards Control:

(a) Electrical equipment must be well insulated, properly grounded, and provided with interlocks and written procedures to minimize sparking and shock exposure. Compliance with OSHA 1910.303, 304, 305, and the National Electrical Code is mandatory.

(b) Fire suppression procedures must take into account the hazardous and flammable nature of the materials present.

(c) Personnel access, evacuation procedures, and drills must be prepared.

(d) Points of Operation. The hazards associated with machinery operation are those created by point of operation, in-going nip points, rotating parts, flying chips and sparks. Machine guards shall be provided to protect operators from these hazards. Compliance with OSHA 1910.211 is mandatory.

(e) Training. All personnel must be trained in approved procedures for dealing with the hazards peculiar to the system or components involved in the operation. The employees shall be thoroughly instructed in the efficient and safe methods of performing their assigned work.

(f) Personal protective equipment consists of garments or devices to protect individuals from specific hazards that will be encountered in the performance of their jobs. These hazards must be kept to the minimum through engineering design or by changes in methods or processes. Sufficient PPE for all involved personnel will be located in the immediate vicinity of any hazardous operation. The operators must have ready access to the PPE and the equipment must be properly maintained.

(g) Life Safe Code. The building or structure being used for the DP shall be provided with exits sufficient to permit the prompt escape of occupants in case of fire or other emergency. The design of facilities shall be such that personal safety will not depend solely on any safeguard that can be made ineffective because of human or mechanical failure.

(3) Safety Requirements and Procedures:

(a) Personnel Protection:

- Limited Access - Number of personnel in area kept to a minimum.

- Signal (flashing light) visible to anyone in the area when hydrogen is being generated.

- Safety shower - eye wash - within 50 ft of hazard source.

- Gas detectors (hydrogen and carbon monoxide with alarm (TBD) (manual or automatic TBD).

- Eye protection.

(b) Facility Protection

- Ventilation fan - (alarm for fan stoppage) in the DP area.

- Ground all electrical equipment.

- Replace glass windows with plastic sash.

- Plastic shielding for personnel.

- Nonsparking tools.

- Emergency lighting.

- PSVs on all pressurized gas lines.

- Local fire extinguishers (dry chemical or carbon dioxide).

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APPENDIX B

APPENDIX B

EXCERPT FROM OPERATING MANUAL

IX. Startup

Refer to P & ID, Drawing No. D-1-MP-1 Revision 4 for the following startup
instructions.

A) Initial Startup

Toyo Engineering's catalysts T-12 and T-48 are used in the High
Temperature Steam Reformer 1-1401 and the Autothermal Reformer 1-2501,
respectively. United Catalysts Incorporation's Cobalt-Molybdenum oxide
(CoMo)-based catalysts are used in the First Stage Shift Reactor 1-2502
and the Second Stage Shift Reactor 1-2503. The T-48 and CoMo catalysts
are introduced into their respective reactors in their oxidized (non-
reactive) state. Catalyst T-48 must, therefore, be activated by being
reduced and the CoMo catalyst must be activated by being presulfided and
reduced prior to normal operation of the test unit. The activation can
normally be accomplished by using nitrogen containing hydrogen and
hydrogen sulfide. However, for this test program, air, steam, and diesel
fuel DF-2 shall be used, as nitrogen and hydrogen may not be available for
startup of commercial units. The diesel fuel DF-2 will be doped with
thiophene ($C_4H_4S$) as deemed necessary to ensure the fuel feed contains the
specified sulfur content of 0.5 wt percent. The startup flow will be at a
reduced pressure and flow rate i.e. 20 to 50 psig and 600 SCFH,
respectively.

The Autothermal Reformer (ATR) 1-2501 is a refractory lined vessel. The
refractory wall shall be dried out prior to be exposed to normal operating
temperature.

A correct slow dryout is essential to maximize the running life of the
Autothermal reformer refractory lining. The period of natural drying at

ambient temperature should be as long as possible, but at least 24 hours to maximize the refractory life. The final dryout period should be at least 2 days, and if possible 4 to 6 days. The longer dryout period is usually preferred, but the vendor will supply a dryout curve and time for the refractory used in the furnace.

A sudden temperature rise in the early stages will result in a hard surface baking of the refractory. As the temperature rise proceeds through the refractory, the last trace of moisture from the cold heater metal wall and the refractory material will turn to steam. Since the steam cannot pass through the hard baked surface, it will force its way out through the refractory. This can result in severe cracking or spalling of refractory, which can mean relining the reformer after removing the severely damaged refractory. Quite often this also results in moving large areas of refractory from the side wall supports.

Refractory dryout will be done in concurrency with the catalyst heatup and activation.

The test unit should be prepared for the refractory dryout and catalyst reduction by establishing normal boiler feedwater (BFW) level in the kettle type Waste Heat Boiler 1-1316 and flow of BFW to 1-1316 from the BFW supply flow of BFW to 1-1316 from BFW supply. Valves V-42 and V-44 shall be opened and under manual control. Flow of BFW shall be allowed to flow to blowdown via the blowdown valve. Cooling water flow is started through the Effluent Cooler 1-1303B and the Steam Condenser 1-1317 by opening valves V-75 and V-64.

Air flow is next started. Prior to beginning air flow through the system, valves, V-2 through V-8, V-10, through V-19, V-78, V-70, V-21, V-23, V-24, V-26, V-28, V-29, V-33, V-35, V-37, V-40, V-41, V-68, V-69, V-46, V-47, V-49, V-51, V-52, V-56, V-66, V-65, V-72, V-74, V-61, V-57 and V-76 are closed. The following valves are opened for initial start-up: V-25, V-34, V-42, V-44, V-60, V-64, V-67, V-75, V-77, V-71, V-73. The Process Air Compressor 1-1803 is started. The air flows through Air Preheater 1-1404,

valves V-25, V-71 and into the High Temperature Steam Reformer (HTSR) 1-
1401. Exiting the HTSR, the air flows through valve V-60 bypassing the
HTSR/ATR Effluent Exchanger 1-1313. It then flows through the Autothermal
Reformer (ATR) 1-2501, the HTSR/ATR Effluent Exchanger, bypass valve V-73
and onto the K.O. Drum 1-1204. Exiting the K.O. Drum, the air continues
its way to the First Stage Shift Reactor 1-2502, bypass valve V-34, the
Second Stage Shift Reactor 1-2503 and into Desulfurizer 1-2504. Exiting
the Desulfurizer, the air flows through the Heat Exchanger Coil 1-1303A in
the Waste Heat Boiler 1-1316, the Effluent Cooler 1-1303B, and into the
Effluent Separator 1-1201. From the Effluent Separator, the air vents to
the atmosphere via Back Pressure Control Valve PCV-18 and lines 3/4"-AA-34
and 2"-EHA-16-P. Once the flow of air is established in the route
described above, the Process Air Compressor operation shall be adjusted to
discharge air flow at the rate of 600 SCFH at 60 psig. Next, the
electrical heaters serving the Air Preheater 1-1404, HTSR 1-1401, ATR
1-2501, K.O. Drum 1-1204, First Stage Shift Reactor 1-2502, Second Stage
Shift Reactor 1-2503 and Desulfurizer 1-2504 are turned on. Current
loadings to these heaters are increased slowly so that the catalyst
temperatures as measured by TI-2 through TI-8, TI-11 through TI-14, TI-20
and T-21 are increased at a rate of 30-40°F per hour.

The catalyst and refractory heatup rate shall be monitored continuously
and temperature readings from appropriate temperature indicators are
recorded, at 30 minute intervals.

As the temperature of the ATR catalyst bed reaches 250°F, this bed
temperature shall be maintained for ten hours. At the end of this holding
period, current loadings to the operating heaters shall be adjusted to
heat the catalysts at an hourly rate of 50°F ATR bed temperature reaches
500°F. This bed temperature shall be held eight hours. Then continue to
heat the catalyst up at a rate of 65°F per hour for the remaining heatup
process.

As temperatures rise and the temperature indicated by TI-20 at the outlet
to First Stage Shift Reactor 1-2502 approaches 570°F, valve V-74 is opened

and the bypass valve V-73 is partially closed forcing air flow through the First Shift Feed Cooler 1-1301. The bypass valve V-73 shall be adjusted to hold the First Stage Shift Reactor Effluent at 570°F as indicated by TI-20.

When the catalyst temperatures in the HTSR and ATR reach 1000°F, valves V-12 and V-78 shall be opened, and Steam Superheater 1-1405 is turned on. Nitrogen is being preheated in Steam Superheater 1-1405 and flows into the HTSR. As soon as preheated nitrogen temperature reaches 1000°F, the steam superheater is ready for the saturated steam. Valves V-78 and V-12 are then partially closed to allow a small flow of Nitrogen to flow through the system together with steam. This is done to ensure that no vacuum is formed in the system due to steam condensate and removal in the effluent Separator 1-1202 prior its exit of the product gas line. Valves V-13 and V-14 shall be opened admitting steam into the system.

When steam starts flowing through the Steam Superheater into the HTSR, the Process Air Compressor 1-1803 is shut down and valves V-25 and V-71 closed.   Valve V-74 is then closed and valves V-73 and V-61 are opened. As valve V-61 is opened, BFW flows to quench the ATR effluent superheated steam prior to its entering the K.O. Drum 1-1204. Valve V-61 shall be adjusted to control the flow of BFW such that the First Stage Shift Reactor Effluent stays at 570°F as indicated by TI-20. Current loading to the Steam Superheater shall be adjusted to achieve a steam superheat temperature of 1000°F initially and then increase the superheat temperature to accommodate a catalyst heatup rate of 65°F per hour. The maximum superheated steam temperature exiting the Steam Superheater shall be set and held at 1300°F. Steam flow rate shall be increased to half the design flow rate and held at 40 lb per hour. Current loading to the electrical heaters of the HTSR and ATR shall be increased continuously until the catalyst temperatures in the HTSR and ATR reach 1800°F During the entire heatup process, a duration of approximately 18 to 36 hours is contemplated, under no circumstance shall the rate of rise of catalyst temperature be more than 65°F per hour.

This heatup process is continued until TI-8 of HTSR reaches 1800°F, TI-14 of ATR reaches 1800°F, TI-20 of the First Stage Shift Reactor reaches 570°F and TI-21 of the Second Stage Shift Reactor reaches 550 °F minimum. When the desired catalyst temperatures are achieved, the catalysts are ready for reduction and pre-sulfidation. Valves in the feed system V-7 and V-10 are opened; Fuel Feed Pump 1-1501 is started and adjusted to deliver 25 percent of the design flow. At this point, the Fuel Feed Pump is pumping DF-2 fuel from the Feed Tank 1-1902 and recycling it back to the Feed Tank via bypass valve V-10. When a steady pump operation is established, a small amount of the DF-2 feedstock is admitted to the HTSR via the small bypass valve V-18 and the HTSR inlet atomizing nozzle for a duration of 2 minutes. The atomized DF-2 fuel is vaporized by being injected into the superheated steam. As the vapor mixture of superheated steam and DF-2 enters the catalyst bed, some reaction steam reforming the DF-2 will take place producing a synthesis gas (syngas) containing mainly $H_2$, CO, $CO_2$, $CH_4$ some light hydrocarbons and some $H_2S$. Hydrogen in the syngas will help to reduce the catalyst and $H_2S$ will presulfide the catalyst. The activated (reduced and presulfided) catalyst initiates further steam reforming reaction of the still unreacted DF-2. The described catalyst activation reactions and DF-2 steam reforming reactions propagate down the HTSR catalyst bed. Though the steam reforming reaction is endothermic, the accompanied catalyst reduction and sulfidation reactions are exothermic. As a result, some temperature rises are expected in the catalyst bed where reduction dominates reforming. These are evident in temperature spikes recorded by the thermocouples TI-2 through TI-8. The syngas and steam exiting the HTSR enters the ATR and reduces the T-48 catalysts. The syngas then flows through the First and Second Stage Shift Reactors reducing and presulfiding the CoMo catalysts. The reduction reactions will be evident in temperature spikes recorded by TI-11 through TI-14 and TI-20 and TI-21. Exiting the Second Stage Shift Reactor, the syngas and steam enters the Desulfurizer for $H_2S$ removal. The ZnO will convert some of the COS to $H_2S$ as well. The desulfurized gas will then be cooled in the Effluent Coolers 1-1303A and 1-1303B prior to venting to atmosphere.

Thermocouple readings throughout the system shall be closely monitored until the temperature spikes pass from the system. At this point, valve V-18 will be opened for another 10 minutes, the DF-2 fuel admission procedure shall be repeated. Intermittent admission of the DF-2 fuel to the system shall be repeated until there is no longer any evidence of temperature spikes. The catalysts are now reduced, sulfided and active. The test run shall be ready for commissioning to normal operation. Continuous exposure of the catalysts to steam alone at elevated temperatures will slowly reoxidize the catalysts. Caution should therefore be taken not to expose the reduced catalysts solely to steam for more than 30 minutes at elevated temperature.

B)  Cold Start Per Catalyst Vendor Recommendations

Cold start refers to starting up the test unit from ambient temperature. All catalysts are in their reduced and active state and are being kept in a nitrogen atmosphere.

Since the catalysts are in their reduced state, air and steam cannot be used as heating media for catalyst heat up. For a commercial unit operation, a storage tank for storing anode effluent gas will be installed. Anode effluent gas will be used as heating media for startups other than the initial startup. For the 2.0 mole per test unit, nitrogen will be used as heating medium since anode gas is not available.

For this cold start process, follow the operating procedures of the initial startup except that nitrogen is used instead of air and steam. Prior to beginning nitrogen flow through the system, valves V-12, V-78, V-25, V-71, V-40, and V-65 shall be opened and valves V-23, V-24, PCV-18, and V-80 shall be closed. Operating status of the other valves in the system are described in the initial startup procedures. At this point, nitrogen is introduced into the HTSR via valves V-12 and V-78 from the $N_2$ gas cylinders. Nitrogen begins to flow through the system in the route described for the initial startup except that it is not vented to atmosphere as valve PCV-18 is closed. Instead, it flows to the startup

recycle line 1"-AA-51 towards the suction of Process Air Compressor 1-1803. The latter is started recycling nitrogen in the route described above. Nitrogen in introduced to the HTSR until the Process Air Compressor operation is established to discharge nitrogen flow at the rate of 600 SCFH at 60 psig. Next, valves V-12 and V-78 are closed and electrical heaters serving Air Preheater 1-1404, HTSR 1-1401, ATR 1-2501, K.O. Drum 1-1204, First Stage Shift Reactor 1-2502, Second Stage Shift Reactor 1-2503 and Desulfurizer 1-2504 are turned on. Current loadings to these heaters are increased slowly so that the catalyst temperatures as measured by TI-2 through TI-8, TI-11 through TI-14, TI-20 and TI-21 are increased at a rate of 50-100°F per hour.

The catalyst heatup rate shall be monitored continuously and temperature readings from appropriate temperature indicators are recorded at 30 minute intervals. As temperature rise and the temperature indicated by TI-33 at the inlet to First Stage Shift Reactor 1-2502 approaches 570°F, valve V-74 is opened and the bypass valve V-73 is partially closed forcing nitrogen flow through the First Shift Feed Cooler 1-1301. The bypass valve V-73 shall be adjusted to hold the First Stage Shift Reactor Effluent at 570°F as indicated by T-20. Current loadings to the electrical heaters of HTSR, ATR and Air Preheater shall be increased continuously until the catalyst temperatures in the HTSR and ATR reach 1800°F and 1400°F respectively. During the entire heatup process, a duration of approximately 18 to 24 hours is contemplated, under no circumstance shall the rate of rise of catalyst temperature be more than 100°F per hour.

C) 8 Hours Cold Startup

Cold startup refers to starting up the test unit from ambient temperature in its cold standby status. All catalyst are in their reduced and active state and are being kept in a nitrogen atmosphere.

The startup operation is the same as the "Cold Start Per Catalyst Vendor Recommendation" described in Section IX B except that the rate of catalyst heatup is somewhat higher.

For startup operation procedures, follow those in Section IX B.  For catalyst heatup, current loadings to electrical heaters of HTSR, ATR and Air Preheater shall be adjusted to attain rise of temperature in catalyst beds at a rate of 100°F per hour from ambient temperature to 400°F and 350°F per hour from 400 to 1800°F.  During the entire heatup process, a duration of approximately eight (8) hours is contemplated.

When the desired catalyst temperatures are achieved, the test unit is ready for normal operation.

D)  3 Hour "Cold" Startup

This startup operation refers to starting up the test unit from its cold (overnight) standby status.  The test operation program is scheduled in certain instance to shut down the test unit after a 16 hour duration run.  The shutdown unit will be depressurized and purged with nitrogen and kept in nitrogen atmosphere at slightly above atmospheric pressure overnight.  All electrical heaters are turned off.  In the following morning, the catalysts temperatures will drop to approximately 1000°F in the HTSR and ATR, and 250°F in the shift reactors and desulfurizer.

The startup operation is the same as the "Cold Start Per Catalyst Vendor Recommendation" described in Section IX B except that the rate of catalyst heatup is somewhat higher.

For startup operation procedures, follow those in Section IX B. For catalyst heatup, current loadings to electrical heaters of HTSR, ATR and Air Preheater shall be adjusted to achieve a catalyst bed temperature of 1800°F in the HTSR and ATR, and 550°F in the shift reactors and desulfurizer.  During the entire heatup process, a duration of approximately 3 hours is contemplated.

E)  Hot Startup

Hot startup refers to starting up the test unit from its hot standby
status.  This startup operation normally takes place after a short
interruption of the process operation while the test unit is being kept
hot and ready for normal operation.

For operation procedures follow the description of the Normal Operation--
steady state in Section X A.

F)  Data Records

Table 9 tabulates the pertinent data points to be recorded during all
phases of startup operation.  Operation data should be taken at 30 minute
intervals.

XI.  Shutdown

A)  Normal Shutdown

During a normal shutdown, the DF-2 fuel and air feed are first terminated,
process steam flow shall be continued for 5 to 10 minutes prior to
complete shutdown.  This is done to avoid any carbon deposition on the
catalyst beds due to the lack of presence of steam.

If the shutdown is to be of short duration, say within 30 minutes, the
catalyst may be kept under normal operating pressure with steam provided
that no condensation of steam would occur.  Heaters associated with all
reactors shall be on and maintained the equipment temperatures to as close
to the operating temperatures as possible.  If the shutdown is to be for
an extended period, the test unit should be depressurized and purged with
pure nitrogen.  (In the case of operating the commercial unit, anode off
gases will be used in lieu of nitrogen).

During shutdown operation, caution must be taken not to allow any synthesis gas to remain in the ATR. the nickel containing catalyst T-48 used in the ATR would form nickel carbonyl $Ni(CO)_6$ with CO under favorable conditions as follows:

o  Nickel is present in an active form--reduced catalyst

o  Carbon monoxide is present in the gas phase

o  High pressure

o  Optimum temperature range for reaction is 210-400°F.

Nickel carbonyl is poisonous to both catalyst and human beings. To mitigate carbonyl formation, the systems will always be purged with nitrogen before cooling.

1)  Hot Standby

During this four week operating program, the operation of test run is expected to be interrupted periodically. This interruption would cause the unit to be shutdown. If the shutdown is of short duration, say within 30 minutes, the catalyst may be kept under normal operating pressure with steam provided that no condensation of steam would occur. If the shutdown is to be of longer than 30 minutes, the test unit should be depressurized, purged with pure nitrogen and kept in a nitrogen atmosphere at slightly above atmospheric pressure. During this period of standby mode, heaters on the HTSR, ATR, Shift Reactors and Desulfurizers shall be on and maintain the equipment temperatures to as close to the operating temperatures as possible.

To start up the system from hot standby, follow the operating procedures described in the Startup Section IX E "Hot Startup."

2) Cold (Overnight) Standby

For a period of two weeks, the test unit shall be run for 16 hours per
day and then shut down for the next day operation. The test unit
shall be placed on cold (overnight) standby after each operating day
shutdown.

The following operating procedures are recommended:

Prior proceed to shutdown, check that a complete set of the final data
set is logged. Then terminate the DF-2 fuel to the HTSR and the air
flow to the ATR by turning off the Fuel Feed Pump 1-1501 and the
Process Air Compressor and closing valves V-19 and V-24. The
superheated steam flow shall be continued for 5 more minutes prior to
shut off. At this point, the back pressure control valve PCV-18 can
be fully opened allowing the system to be purged with nitrogen.
Valves V-14, V-10, V-61, V-73, V-34 and V-68 shall be in their closed
positions. Valves V-12, V-78 and V-11 shall be opened admitting
Nitrogen from nitrogen gas cylinders into the system and purge through
PCV-18 for 15-20 minutes.

At this point, nitrogen can be admitted into the system with PCV-18
closed. Electrical heaters on HTSR, ATR, K.O. Drum, Shift Reactors
and Desulfurizer are turned off. The system can be held at cold
(overnight) standby mode with nitrogen at slightly above atmospheric
pressure. To start up the system from cold (overnight) standby,
follow the operating procedures described in the Startup Section IX C
(8 hours Cold Startup).

3) Cold Standby

For the second, third and fourth weeks operation, the test unit shall
be run for 16 hours on the last day and then shut down for the
weekend. The test unit shall be placed on cold standby and be ready
for startup the following Monday morning.

The operating procedures for this operation are the same as those described for the cold (overnight) standby mode in Section XI A2.

B)  Complete (Extended) Shutdown

Complete shutdown should not be undertaken unless it is required to replace catalysts or to perform equipment maintenance. Since the catalysts are in their active (reduced) state and are pyrophoric, the catalysts will have to be deactivated prior to their exposure to atmosphere.

For complete shutdown of the test unit, follow the normal shutdown--cold (overnight) standby procedures, described in Section XI A2, up to the nitrogen purge step. At this point superheated steam instead of nitrogen is used to purge the system. All the heaters shall be on if necessary to maintaining the HTSR catalyst bed, ATR catalyst bed above 1000°F and the shift catalyst beds and ZnO bed above 500°F. A small flow of air (5 percent of normal flow rate) is admitted to the HTSR via the bypass valve V-26 and Valve V-71 for a period of 2 minutes. Similar to the reduction procedure, the exothermic heat of oxidation will be reflected in a series of temperature spikes. Thermocouples TI-2 through TI-8, TI-11 through TI-14, TI-20 and TI-21 are monitored closely until all of the temperature spikes have passed through the system. When the system temperature profile returns to normal, a small flow of air is admitted to the HTSR via the bypass valve V-26 and valve V-71 for a period of 2 minutes once again. This procedure is repeated each time after the temperature spikes vanish until there is no longer any system response to the admission of air. At this point the catalysts are considered oxidized and deactivated. It can then be purged with air and all the heaters can be turned off. The system will then be allowed to cool down to ambient temperature.

C) Emergency Shutdown

Emergency shutdowns may be caused by equipment failure, utility failure or by maloperation of the plant. The following describes some of the predicted potential emergency shutdown situations and essential procedures to shutdown the demonstration unit to avoid catalyst and/or equipment damage.

1) Loss of process steam.

In the event of loss of process steam due to any reason, the demonstration unit must be shutdown immediately to avoid carbon deposition on catalysts. The following shutdown procedures must be carried out immediately.

A) Trip Fuel Feed Pump 1-1501

B) Open valves V-78, V-12 and PCV-18 admitting $N_2$ to purge the system.

C) Shut down Air Preheater 1-1404

D) Close Valve V-24

E) Finally follow the normal shutdown procedures as described in Section XI A 1,2, or 3 depends on the current situation.

2) High temperature runaway in the ATR 1-2501.

In the event of occurrence of temperature runaway in the ATR, control valve FV-5 will be tripped and closed automatically. The demonstration unit must be shutdown immediately. The following shutdown procedures must be carried out immediately.

A) Trip Fuel Feed Pump 1-1501

B) Shutdown Air Preheater 1-1404

C) Close Valve V-24

D) Finally follow the normal shutdown procedures as described in Section XI A 1,2 or 3 depends on the current situation.

In general, in an emergency, it should be endeavored to reduce the status of the plant to that corresponding to some phase of the initial startup or normal shutdown operation. At that time, circumstances will dictate whether to continue in the startup sequence or in the shutdown sequence.
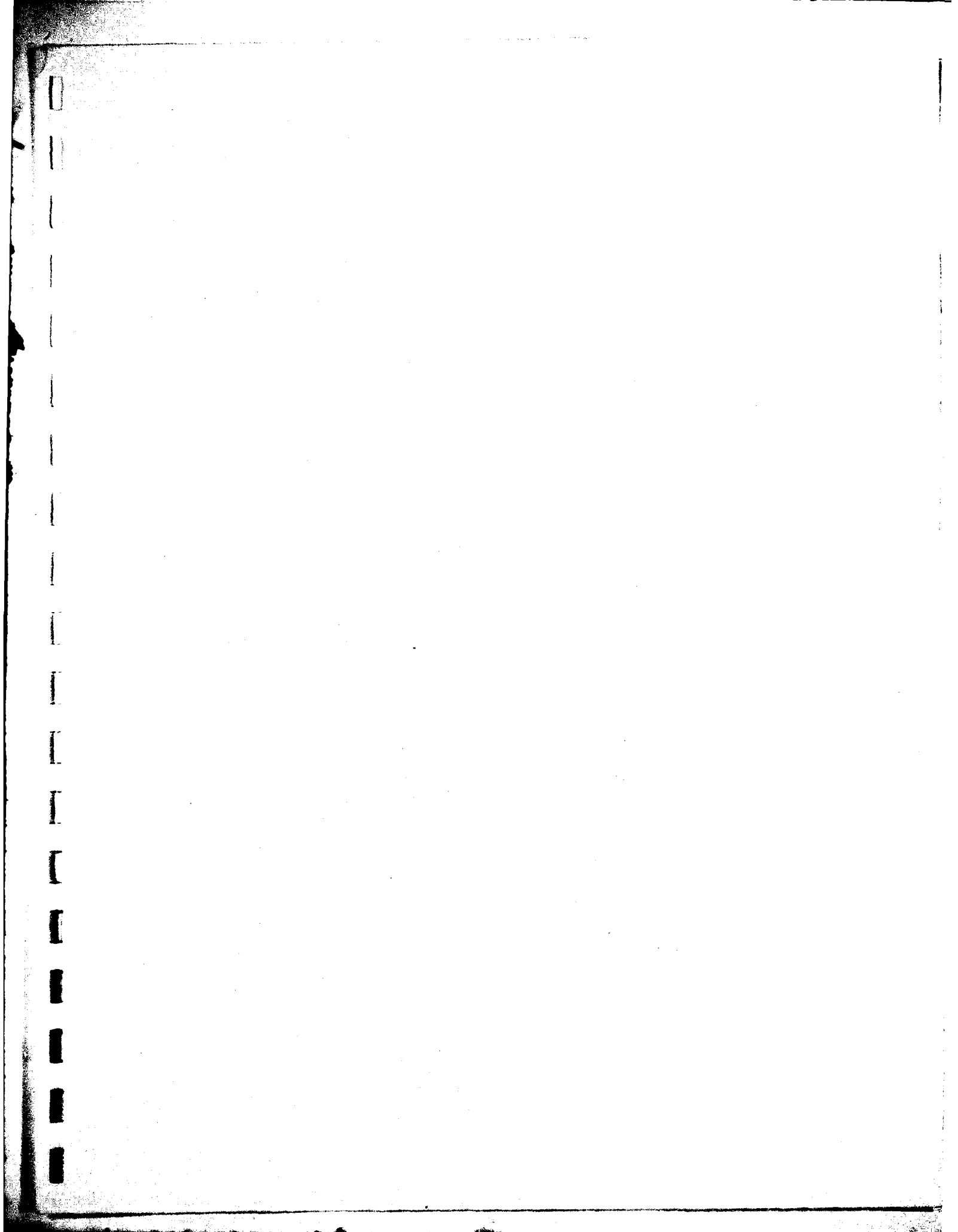
# APPENDIX C

## DF-2 AND FEEDWATER ANALYSIS

1. DF-2 ANALYSIS:

| Determination | ASTM Method | Specifications | Results |
|---|---|---|---|
| 1. API Gravity at 60°F | D287 | 32.0 - 38.0 | 34.5 |
| 2. Cloud Point, °F | D2500 | 24 Max | 13 |
| 3. Distillation 90% evaporated, °F | | 640 max | 626 |
| End Point, °F | | 700 max | 673 |
| 4. Water and Sediment, Volume % | D1796 | 0.05 max | 0.05 |
| 5. Flash Point, °F | D93 | 140 min | 130 |
| 6. Ash, % | D482 | 0.01 max | 0.00010 |
| 7. Carbon Residue, % (on 10% bottoms) | D524 | 0.35 max | 0.10 |
| 8. Viscosity at 40°C | D445 | 1.9 to 4.1 | 3.18 |
| 9. Sulfur, % | D129 | 0.7 max | 0.042* |
| 10. Copper Corrosion (3 hr. at 212°F) | D130 | No. 2 max | 1A |
| 11. Cetane Number | D976 | 40 min | 49.8 |
| 12. Oxidation Stability (accelerated method), mg/100 ml | D2274 | 2.0 max | 0.4 |
| 13. Pour Point, °F | D97 | 15 max | 8 |
| 14. Particulate Contamination | D2276 | | |
| Total Contaminant, mg/L | | 10 max | 0.4 |
| Ash Residue, mg/L | | 1.3 max | 0.4 |
| 15. Gross Heat of Combustion, million Btu/Barrel | D240 | 5.7 min | 5.76 |
| 16. Total Acidity, mg KOH/gm | D974 | -- | 0.008 |

*Sulfur content as received. The as-received DF-2 was "spiked" with thiophene to achieve a 0.5 weight percent sulfur content in the demonstration plant DF-2 feed.

| Determination | ASTM Method | Specifications | Results |
|---|---|---|---|
| 17. Aniline Point, °F | D611 | -- | 69.5 |
| 18. Cetane Index Ignition Quality | D613 | -- | 43.4 |

2. WATER ANALYSIS:

| Determination | Concentration/Result |
|---|---|
| Total Solids | <310 mg/L |
| Total Suspended Solids | <0.4 mg/L |
| Total Dissolved Solids | 309 mg/L |
| Iron | 0.03 mg/L |
| Lead | <0.03 mg/L |
| Tin | 0.04 mg/L |
| Chlorine | 58.6 mg/L |
| Bromine | 35 mg/L |
| Fluorine | 0.15 mg/L |
| Iodine | <0.1 mg/L |
| Sulfur | <0.02 mg/L |
| Coliform Type Bacteria | <2.2 -/me |
| Conductivity | 790 $\mu$mho/cm |

# DATE FILMED